

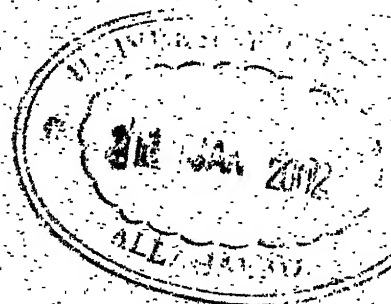
STUDIES IN SYNTHESIS AND ANALYTICAL ASPECTS OF SOME NATURALLY OCCURRING MINERALS

(Applications of Ion Selective Electrodes)

Thesis Submitted For The Degree of

DOCTOR OF PHILOSOPHY

Chemistry



By

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ॐ शुक्लां ब्रह्मविचार सारपरमा माद्यां जगद्व्यापिनीं ।
वीणा पुस्तक ६॥शिखोऽभ्युदयदां जाड्यान्धकाराप्रहाम् ॥
हस्ते स्फटिमालिकां विदधतीं पद्मासने संस्थितां ।
वन्दे त्वां परमेश्वरीं भगवतीं बुद्धिप्रदां शारदाम् ॥



Dedicated to,

My Beloved Parents

Shri Pt. Mohan Chandra Joshi

and

Smt. Janki Mohan Joshi

who encouraged me to proceed along a path

"Where tireless striving stretches

its arms towards perfection"

With Deep Regards

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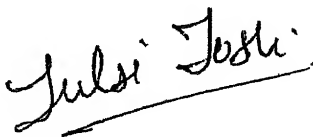
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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	Percentage
λ	Wavelength
$^{\circ}\text{C}$	Degree celcius
AAS	Atomic Absorption Spectroscopy
a_i	Activity of primary ion (i)
a_j	Activity of interfering ion (j)
c	Concentration
Calc.	Calculated
C_i	Concentration of species, i
cm	Centimeter
CWISE	Coated Wire Ion Selective Electrode
dil	Dilute
E	The experimentally observed potential of a cell (in millivolts)
E°	Standard potential
e.m.f.	Electro motive force
F	Faraday constant (96485 C mol^{-1})
Fig.	Figure
g	Gram
h	Hour
I_i	Current (flux per g ion)
ISE	Ion Selective Electrode
K'	Absorption coefficient
Kb	Kilobar
K_{ij}	Potentiometric selectivity coefficients, i for primary ion, j for interfering ion
l	Path length
LISE	Liquid Ion Selective Electrode
m	Molality
max	Maximum
MISE	Membrane Ion Selective Electrode
ml	Milliliter
mV	Millivolt
N	An integer corresponding to electron charge in electrode reaction

nm	Nanometer
obs.	Observed
ppm	Parts per million
PVC	Poly Vinyl Chloride
R	Gas constant ($8.31441 \text{ JK}^{-1} \text{ mol}^{-1}$)
R.I.	Reflective Index
SCE	Secondary Calomel Electrode
Sec	Second
T	Thermodynamic temperature ($^{\circ}\text{K}$)
wt.	Weight
XRD	X-Ray Diffraction
XRF	X-Ray Fluoresence
Z_i	An integer with sign and magnitude corresponding to charge of principle ion, i

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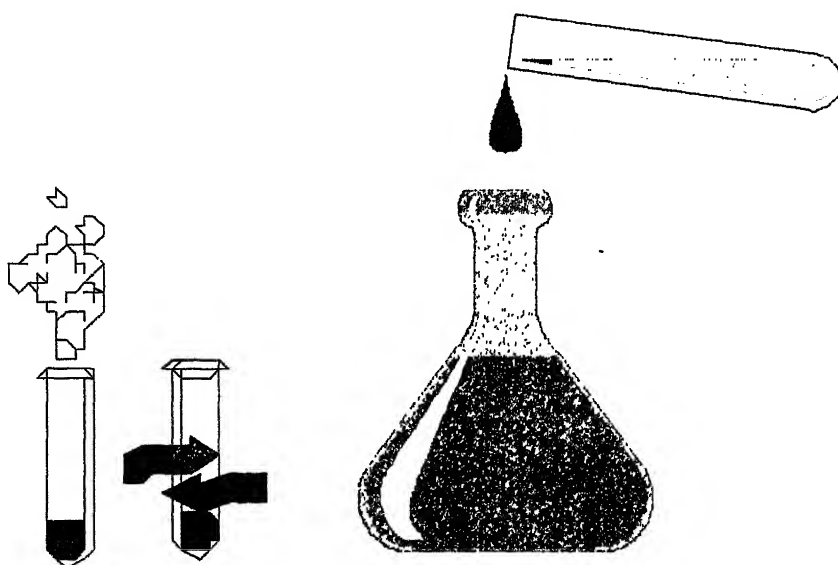
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2. Determination of pH, Dissolved Oxygen and Iron in Water. "Soil Fertility and Environmental Symposium", Allahabad (1997).
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8. Determination of Zn (II) Ion in Naturally Occurring Minerals by using Zn (II) ISE. Indian Chemical Society 1999 (Communicated).
9. Determination of Ca (II) Ion in Naturally Occurring Minerals by Ca (II) ISE. Environmental Geochemistry 1999 (Communicated).
10. Determination of Mg (II) Ion in Dolomite. Indian Chemical Society 1999 (Communicated).

CHAPTER 1

Introduction



INTRODUCTION

1.1 ANALYTICAL CHEMISTRY (History, Scope and Applications)

Analytical chemistry may be said to be as old as the science of chemistry itself. As knowledge developed, man wanted to know more about his own surroundings and thus chemists attempted to analyze air, water and minerals which led to the development of analytical methods. Analytical studies, as different from methods, which are preparative, resulted in the change of attitude from magic and alchemy to a quantitative and scientific approach. This was ultimately responsible for the rejection of the Phlogiston Theory and led to the foundation of the laws of chemical combination and to the enunciation of Dalton's atomic theory.

The closing years of nineteenth century and the first couple of decades of the present century witnessed remarkable discoveries in various scientific disciplines and chemistry being useful to all of them was regarded as the handmaid of sciences. Chemistry provided the materials, techniques and view points for proper understanding in areas of physics, geology, biology, agriculture and medicine. The analytical chemistry automatically became the handmaid of chemistry, since it provided information on the materials being handed.

Analytical chemistry as an independent discipline may be said to have been recognized in 1853 when Wilhelm Ostwald published the first book on the subject entitled, "Die Wissens Chaftlichen Grundlagen der analytischen Chemie." In 1862 the first journal devoted to analytical chemistry was published from Fresenius's Laboratory, which was entitled, "Zeitschrift für analytische Chemie." This provided an impetus to researchers in analytical chemistry at various centers. Soon institutes of analytical chemistry were founded in Germany, Austria and other

countries of mid- Europe and also in U.S.A. The journal "Analyst" had commenced publication in Great Britain in 1877.

Today analytical Chemistry is considered to be not only as a handmaid of chemistry but has a status of importance in its own right. The analytical chemistry today would include not only the quantitative and qualitative analyses but also the characterization of a variety of materials including their structural studies.

As we now know, that no other branch of science finds so extensive except the application of analytical chemistry purely for two reasons. One finds numerous applications in various disciplines of chemistry such as inorganic, organic, physical and biochemistry and secondly, it finds large applications in other fields of sciences such as environmental sciences, agricultural sciences, naturally occurring minerals, biomedical and clinical chemistry, solid state research and oceanography, forensic sciences, space research and synthetic materials. Naturally occurring materials like zeolitic tuffts have been used by man for more than two thousand years as light weight dimension stone and in pozzolanic cements and concrete's, however, it has been only within the last 5 decades that the zeolite contents of many of these materials has been recognized. The hundreds of discoveries of high-grade zeolite deposits in sedimentary rocks of volcanic origin since 1950 has led to the development of a host of applications which take advantage of the low mining costs of the near surface deposits and of the attractive physical and chemical properties of zeolite structures. The use of naturally occurring zeolite is increasing. However, the applications of synthetic material take precedence over the naturally occurring materials due to low mining cost. Further to reduce the cost of such materials one needs low cost analytical techniques for the analysis and monitoring of such synthetic materials like zeolite.

The analysis of micronutrients such as iron, copper, zinc, potassium, molybdenum, boron, and manganese by spectrophotometry is a common example of application of analytical techniques in soil samples. In the field of biomedical research and clinical chemistry, one can cite several examples, like analysis of barbiturates, food poisoning, presence vanadium, arsenic in hair and nail by spectroscopic methods. Analysis of cobalt in vitamin B₁₂, iron in hemoglobin of blood, and their isolation by electrophoresis or gel permeation techniques etc. In the field of electronics, the analysis of traces of elements such as germanium in semiconductors and transistors, determination of selenium, caesium ion photocells is possible by newer methods like emission spectroscopy or neutron activation analysis. In the field of oceanography, earth sciences and planetary sciences, analytical chemistry extensively being used. The chemical analysis of sea water, analysis of basaltic rocks for presence of manganese and aluminium or the rapid analysis of elements from minerals. All these illustrations amply show that analytical science is truly an interdisciplinary area of research.

1.2 SELECTIVITY IN ANALYTICAL CHEMISTRY

The problem of selectivity is of prime importance in the domain of analytical chemistry. The problem acquires greater importance at low concentration where potential interference might be present at substantially higher concentrations than the analyze of interest. Instrumental techniques, over the past three decades as so have helped in achieving greater selectivity at trace levels. These techniques include gas chromatography, liquid chromatography, atomic absorption and mass spectrometry for organic compounds and inductive couple plasma emission spectroscopy for metals. Prior to the development of such sensitive techniques, selectivity was usually achieved by means of selective chemical reactions.

The present century saw the selectivity phenomenon being observed in the areas of electrochemical sensors which subsequently resulted in the development of a large number of selective ion sensitive electrodes (ISE). An important advantage of these types of sensors is that they can, in principle, be designed for any ionic species. The other advantage in the use of these sensors are:

- (i) Analysis is simple,
- (ii) Real time analysis,
- (iii) Large dynamic range,
- (iv) Simple instrumentation and
- (v) Small size.

From the analytical point of view such electrodes represent a suitable means for determining different ions, owing to their ability to monitor selectively and continuously the activity of a particular ion in a solution. The applications of these sensors are ever increasing in direct potentiometric determinations, biopotentiometric and potentiometric titrations, kinetic studies, resolution of reaction mechanisms, biomedical research, oceanographic, rock, mineral and soil analysis studies etc. The applications of ISEs in industrial analytical control are also promising.

1.3 FEATURES OF ION SELECTIVE ELECTRODES

The history of ion sensitive electrodes goes back to 1906, when Cremer (1) for the first time designed a membrane electrode, which was selective to a particular ion, and this electrode was glass electrode. Harber and Klemensiewicz (2) described a highly selective probe for measuring pH. This glass electrode was used together with a reference electrode and pH meter, formed a useful analytical technique that was to completely revolutionize the field of chemical analysis of ion species both cations as well as anions. This new trend was conditioned by the

advantages of the ion selective electrode (ISE) system-selectivity, sensitivity (to 10^{-5} M or lower), reliability, low cost, speed of analysis, and the fact that the sample is not destroyed or consumed in the process.

However, the entire field lay dormant for 60 years, due to a misconception of the function of the pH electrode probe. If indeed, the theoreticians were correct in their premise that the mechanism involved. A critical migration of H^+ ions across a membrane interface to the opposite side where measurement was effected, then only a glass H^+ ion electrode would be possible only H^+ is small enough and diffuse enough to transverse the membrane. This was shown not to be true in the 1960s and a deluge of ion probes resulted. As a result of this incisive work by Karreman and Eisenman (3) and Stephanova and co-workers (4), probes for many ions, such as, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cd^{2+} , Ag^+ , NH_4^+ , S^{2-} , I^- , Br^- , Cl^- , CN^- , SCN^- , F^- , NO_3^- , ClO_4^- , BF_4^- and others, are available today from several manufactures.

In 1972 Buck (5) wrote a review article for Analytical Chemistry citing more than thousand references in the field of ion selective electrodes. This was followed by another review article of Koryta (6) in which theoretical considerations for the interpretation of various types of ISEs are dealt with and more than 700 references have been cited in this article. The same year one saw other review articles appearing in various journals (7-15).

In the seventh decade of the century a number of reference books dealing with different aspects of ISEs were published (16-21). Pergmon Press in 1979 introduced a review journal "Ion Selective Electrode Reviews" whose name was subsequently changed to "Selective Electrode Reviews". A number of pioneer workers like Hulanicki, Pungor, Buck and others started certain international conferences on ISE. The first conference was held in *Czechoslovakia* and ever since that every four

year this conference has been organised at Matrafured, Hungry. The eighth international conference on ISE was held at Matrafured, Hungry during 14 to 18 October 1998 in which more than 100 scientists from all over the globe, working on the various aspects of ISE participated.

On going interested in the research of ISE is reflected in the review articles which are appearing in the literature at a regular intervals (22-24). The popularity of technique can be gazed by the fact that number of standard text books on Analytical Chemistry have included chapter on ISEs.

1.3.1 Precipitate Based Ion Selective Electrodes

With the fundamental work of Nicolsky (25) concerning the interpretation of the potential response of glass electrodes through ion-exchange theory, a completely new idea had been introduced initiating research on the development of novel ion sensitive electrodes. Natural and synthetic zeolites had first been studied as electrode materials and these investigations led to the discovery of ion exchanger as well as complex forming legand based ion-selective electrodes.

In the 1930s attempts were made to study the inorganic precipitates also as electrode materials. Among others, barium suphate has been used and it was found that according to the theory of Teorell (26) and Mayer and others (27) only a diffusion potential had developed and been measured between the two boundary phases of barium sulphate based membrane. Kolthoff and Sanders (28) prepared silver chloride pellet based electrodes, which were used successfully to follow potentiometric precipitation titration.

A systematic work on the precipitate based ion-selective-electrodes were initiated by Pungor and co-workers in the institute of General and Analytical Chemistry, Technical University of Budapest, Hungary. They

also wrote chapters on precipitate based ion-selective electrodes in different books (21, 29).

From the theoretical consideration it was further concluded that the electrode materials that finally proved to be most successful were inorganic precipitates and neutral complexing agents. They worked out theoretical aspects of such electrodes (30). They concluded that "Since the middle at the sixties we have always emphasized that every electrode which works on the basis of a precipitate exchange reactions should be called a precipitate based electrode."

1.3.2 Heterogeneous Membrane Ion Selective Electrodes

Since the present work is concerned with electrodes prepared from heterogeneous membranes, a brief account of these membranes is desirable. Membranes of these types are prepared by dispersing ground-dried powder of metal salts, chelates, ion-exchangers and macro-cyclic compounds in inert matrices. The physical properties of these active materials (e.g. grain size, crystalline form, conditions of precipitation etc.) are important for the functioning of the membrane. When barium sulphate and silver chloride precipitates are used as electroactive materials, they should be obtained by precipitation in the presence of excess of sulphate and chloride ions respectively. In the case of lanthanum fluoride and silver bromide, the precipitation should be performed in the presence of excess of lanthanum and silver ions respectively (31-34). Examination of the standard potentials shows that silver halide electrodes have standard potentials typical of those expected for material saturated with elemental silver. The one exception occurred when a silver bromide membrane was deliberately saturated with the bromine during preparation contacted with carbon (35). Contacting the same membrane with silver fairly rapidly saturated the silver bromide with silver metal (33). Membrane electrodes with electrolytic internal

contacts may have quite different standard potentials, depending on the choice of electrolyte and inner reference electrode.

In case of metal sulphide electrodes, the carbon-contacted electrodes have standard potentials typical of those expected for sulphur saturated electroactive components and are distinct from silver-contacted membrane electrodes. In the preparation of sulphide precipitates, the sulphide ion in solution is easily oxidised and incorporation of sulphur in the precipitate may be envisaged. Contact with silver metal presumably results in eventual saturation with silver, although the recorded standard potentials are rather higher than expected.

For developing the heterogeneous ion selective electrode it is essential to place the electroactive material in an inert matrix. Matrix material should be such that it neither undergoes any reaction with the electroactive material nor with the test solution. Silicone rubber, epoxy resins, polyvinyl chloride etc. are some of the materials which are in use for working heterogeneous ion selective membranes.

1.3.3 Choice of Electroactive Components

The single most important factor in optimizing ion sensitive electrodes concerns the choice and development of selective electroactive components. Thus, the origin of the successful commercial ISEs lies in the use of materials with proven selectivity in solvent extraction work, such as dialkyl phosphates for Ca ISEs and long aliphatic chain quaternary ammonium salts for nitrate and perchlorate ISE's. There is a close relationship between electrode selectivity coefficients K_{ij}^{pot} and competitive ion pair extraction constants ($E_{Q^I}/E_{Q^{II}}$) for Q^{II} extractant (36-37). Earlier studies on naturally occurring ionophores e.g. valinomycin for potassium ISE has been followed by the synthesis of improved

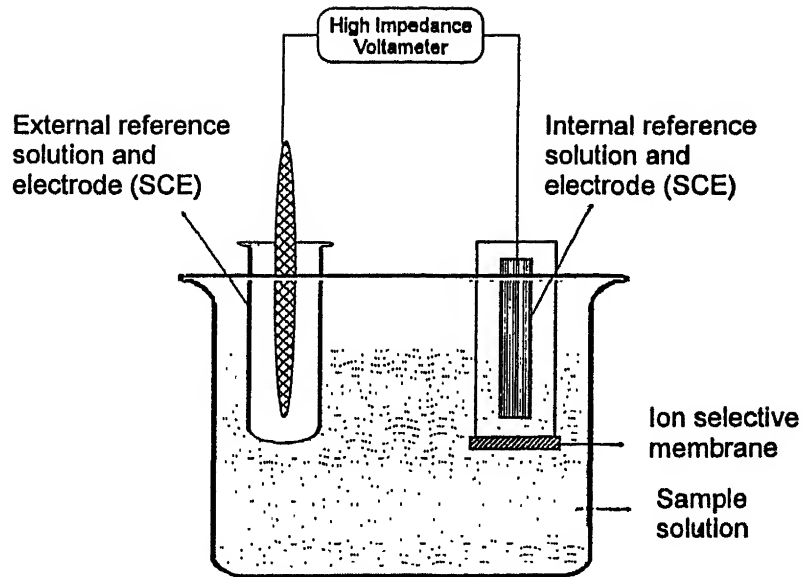
materials and organic ionophores with highly selective complexing properties for certain ions.

Inorganic precipitates also act as excellent electroactive materials for the preparation of membrane electrodes. The theoretical interpretation of electrochemical behaviour of such precipitate based electrodes is fundamentally based on solubility equivalent and precipitate exchange reactions existing at the phase boundaries of the electrode membrane (38, 39), because these are significantly influenced by the morphology and different structure of the precipitates. The concentration of the defects of the electrode membrane is worth considering in describing the electrode potential, since these defects are likely to influence the potential.

1.3.4 Principles of ISE's Measurements

Ion selective electrodes, has been stated above consists of a membrane, which are composed of either a solid or liquid phase permeable only to one ion species, incorporating an electroactive material. These electrodes utilize an internal solution of constant composition in contact with membrane and an internal reference electrode. When the ISE is placed in a solution containing the particular ion a small number of ions pass from the solution of higher concentration through the membrane to that of lower concentration, thus producing an electric potential difference. Consequently the trans membrane difference of electrode potential is generated which eventually stops further diffusion of the particular ion species. An electric double layer simultaneously formed on both sides of the membrane (Fig. 1.1).

The equilibrium between the solution and the membrane phase is attained when the difference of the two electrochemical potential between the solvated ion (η_i) and the ion bonded to the membrane (η_s) equals zero. The ion on the membrane is not considered, it normally has no effect on the membrane potential at zero current.



Schematic diagram depicting the experimental assembly required for making potentiometer membrane electrode measurements

FIG. 1.1

Therefore, the electrochemical potential in the solution is:

$$(\eta_i) + (\mu_i) + ZF\psi_i \quad \text{--- (1)}$$

and the electrochemical potential across membrane is:

$$(\eta_s) + (\mu_s) + ZF\psi_s \quad \text{--- (2)}$$

where, n is the electrochemical potential

μ is the chemical potential

Z is the valency of the test ion

F is the Faraday constant

ψ is the Galvani potential

At equilibrium $\eta_i = \eta_s$, and

$$\mu_i + ZF\psi_c = \mu_s + ZF\psi_s \quad \text{--- (3)}$$

$$ZF(\psi_s - \psi_i) \mu_i - \mu_s = \mu_i^\circ - \mu_s + RT \ln (a)_i / (a)_s \quad \text{--- (4)}$$

μ_i° being the standard chemical potential. Equation 4 then becomes

$$E = E_0 + RT/ZF \ln (a)_i / (a)_s \quad \text{--- (5)}$$

Where, E is the electrode potential, E_0 is the standard electrode potential, a_i and a_s are the respective activities of the ion in solution and the membrane phase.

Since the electrode contains an internal solution of constant composition, the electrical potential measured using such a half-cell depends solely on the activity of the ion in the external test solution. Therefore,

$$E = E_0 + RT/ZF \ln a_i \quad \text{--- (6)}$$

All the junction potentials participating in the net e.m.f. are taken as constant except that which depends on the nature of the test solution.

Several points need to be considered when carrying out measurements using ISEs in order to obtain the activity of ionic species for use in ionic association calculations. These involve the experimental set-up consisting of the ISE of the ion under consideration, the reference electrode, the cell and the millivolt-meter. Also, there are volumes, concentrations and pH values of the solutions for which activities are needed. The temperature at which measurements is desired is also important, as well as the choice of standards. Above all, the proper experimental procedure is very important in obtaining reproducible and dependable results.

When ISEs are used to monitor chemical reactions, the monitored parameter is always the electroactive force of the cell (40).



For simplicity, hereafter, this parameter will be called "electrode potential" and will be symbolized by E .

If the analyte contains interferent j with activity a_j the ISE membrane potential will be given by

$$E_{ISE} = \text{Const} + 2.303 \frac{RT}{ZF} \ln [a_i(I) + K_{ij}^{\text{Pot}} a_j(I)] \quad \text{--- (7)}$$

where K_{ij}^{Pot} is a selectivity coefficient of ISE for ion i with respect to ion j. This equation 7 was first put forward by Nikolosky and is known as Nikolosky equation. The equation indicates that the lower the value of selectivity coefficient smaller is the interference due to j.

1.4 THE PRESENT WORK

In the electrochemical sensor laboratory in the Department of Chemistry University of Allahabad, Chattopadhyaya and co-workers (41-68) during the last twenty years, have been working on new electrochemical sensors. A systematic work is in progress for designing new sensors and their applications in various areas of analytical chemistry, including determination of cations and anions, assay of drugs and biochemical substances, and also the study of metal ligand equilibria in solution.

The present work is a part of the programme on the development of some novel sensors for the analysis of soils, minerals and synthetic materials.

Soil is a poly-phase system composed of solid particles, water and air. The solid particles carry variable amounts of negative and positive charges and can adsorb cations and anions on their surfaces as counterions. Under neutral conditions some of these ions will dissociate in the soil water. These ions together with ions arising from dissolution of the solid phase and these ions brought in by fertilizers are the sources of plant nutrients. Therefore, the behaviour of ions in soil is the focus of soil chemical studies.

Due to the interactions between ions and clay particles, the actual quantity, i.e., the activity of ions in a soil which is of concern in relating ions to plant growth and in interpreting many chemical processes in soils cannot be simply treated as in solution chemistry. However, ion selective electrodes, which respond to ion activities can fulfil this demand in soil chemistry. In this respect it can be said that no other means can take the place of ion selective electrode measurements in many soil studies, It is therefore, no wonder that in soil science potentiometric methods have been extensively used.

As early as 1939, C. E. Marshall of the University of Missouri made mineral membrane electrodes from zeolitic thin plates (69). These may be considered as prototypes of ion-selective electrodes. They were responsive to monovalent and divalent cations. Later, Marshall made electrodes responsive to mono and divalent cations or to monovalent cations alone by treating clay membranes at different temperatures. In this way he carried out much fruitful research work in soil chemistry.

In the last twenty years, the application of ion-selective electrodes in soil science has increased rapidly and a literature survey shows that papers relating to the use of ion- selective electrodes in soil science number more than three hundred. Short reviews of the field have been given Carlson and Keeney (70), by Zhang (71) and later on by Talibudeen and Page (72).

The ion-selective electrodes have also been used in the analysis of minerals. The clay membrane is prepared (73,74) by evaporating a suspension of the colloid fraction (less than 0.2 μm) of suitable clay, such as, bentonite or beidellite to a membrane of 0.2-0.3 mm thickness. Most of the studies devoted to applications of ion-selective electrodes in soil science and mineral science relate to their use as analytical tools in the determination of ions.

The present thesis is primarily concerned with the fabrication of some new ISEs for their possible applications in the analysis of naturally occurring minerals and soils samples.

Crystalline zeolites are unique adsorbent materials. In recent years zeolite minerals have found increasing application in the field of pollution abatement, and they are fast becoming standard components in the design and construction of such facilities. Both the ion exchange and adsorption properties of zeolites can be utilized, however, most applications that have been developed are based on the ability of certain zeolites to exchange large cations selectively from aqueous solutions.

In 1959, L.L. Ames of Hanford Laboratory of Battell-Northwest, Richland, Washington, demonstrated the ion-exchange specificity of clinoptilolite for the removal of cesium and strontium from low-level waste streams of nuclear installations (75-77).

Another area of pollution control involves the use of natural zeolites in the removal of SO₂ and other pollutants from stack gases of oil and coal-burning power plants (79-81).

A novel use of zeolites in pollution control is as a sorbent in oil-spill cleanup. Miki *et. al.* (82) pelletized a mixture of activated zeolite, expanded perlite, sodium carbonate, tartaric acid, and a binder consisting of 20% methylsiloxane solution.

Although the use of zeolites in coal gasification may be some years in the future, natural zeolites have been employed successfully since 1968 to remove CO₂ from contaminated and sour natural gas (83).

Zeolites might also make contributions in the solar energy field (84). Natural zeolites have shown to be potentially useful in the purification and production side of the business. Mordenite, chabazite and clinoptilolite are generally capable of withstanding the rigors of continuous cycling in acid environments and have been used

successfully to remove water and carbondioxide from gaseous hydrocarbons (85).

Similar to their synthetic counterparts, the high ion exchange and adsorption capacities of many natural zeolites make them effective carriers of herbicides, fungicides and pesticides. Yoshinaga *et. al.* (86) found clinoptilolite to be an excellent carrier of benzyl natural zeolites as a base, Hayashizaki and Tsuneji 1973 developed a lime-nitrogen acaricide with good results.

Not only can the ion-exchange properties of certain zeolites be used to carry nutrient ions into soils, they can also be exploited to trap undesirable cations and lessen their introduction into the food chain. Fujii in 1974 (87) found that pulverized zeolites effectively reduced the transfer of fertilizers added heavy metals, such as Cu, Cd, Pb and Zn from soil to plants. Several workers (88-91) have noted the selectivity of clinoptilolite for such heavy metals.

Since 1965, experiments have been in progress in Japan on the use of clinoptilolite and mordenite as dietary supplements in animal husbandry. Up to 10 % zeolite has been added to the normal rations of pigs, chickens and ruminants resulting in significant increases in feed-conversion values and in the general health of the animals.

In the present work an attempt has been also made to synthesize zeolite and characterise the same. The thesis has been divided into 7 chapters.

Chapter 1 forms the general introduction the subject matter in which the importance of analytical aspects of naturally occurring minerals and related materials has been dealt with. The importance of analysis with ISEs has been under lined. The aim of the present work has been included at the end of this chapter.

The chapter 2 deals with the technique and methodology used in the present work. A brief outline of fabrication of ISEs, studies of their characteristic etc. has been represented. The instrumental methods such as X-ray, XRF, Hydrothermal and Atomic Absorption Spectroscopy, which are used in the present work, have been dealt in brief.

The synthesis of zeolite and related experimental details has been described in chapter 3. The synthesis of various electroactive materials used for fabrication of ISEs has been described in this chapter.

Chapter 4 deals with the design and characteristics of K (I), Ca (II), Mg (II) ISEs and their applications in *limestones, calcite, chalk, dolomite, magnesite* and six different *soils* samples.

In Chapter 5 the construction of Al (III) and Pb (II) ISE's together with their characteristics have been presented. The work on application of these electrodes in the analysis of *bauxite, clay, laterite, marl, alum, galena, red lead* and six different *soil* samples has been also described in this chapter.

Chapter 6 deals with the designs and characteristics of Cu (II), Zn(II), Mn (II) and Fe(III) ISEs and their applications in analysis of *copper pyrite, zinc-blende, calamine, manganite, haematite* and six different *soils* samples.

Finally the total work done together with meaningful results obtained and various conclusions drawn has been summarized in chapter 7 in the last, the total work as well as conclusion and the meaningful results obtained has been summarized in chapter 7.

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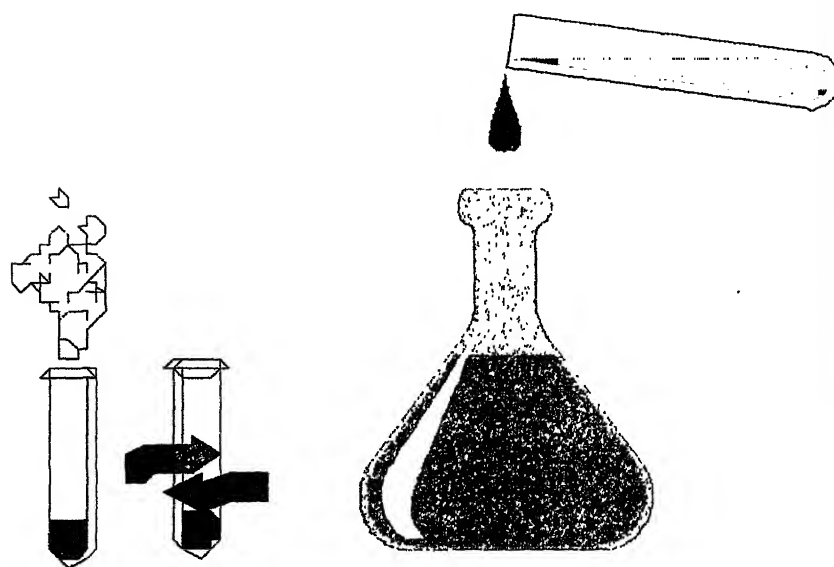
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CHAPTER 2

Material, Method and Techniques



MATERIAL, METHOD AND TECHNIQUES

2.1 INTRODUCTORY

It has been said earlier in chapter 1 that the main emphasis of this thesis is the use of ISEs in the field of naturally occurring minerals and soil samples. Hence, a detailed account of the ISE as a tool for determination of cations has been presented.

A number of other methods such as Gravimetric, Volumetric, Spectrophotometric etc. are well known for the analysis of minerals, ores and soil samples. But ISEs are in many respects ideal sensors for use in the analysis of industrial samples, naturally occurring minerals and soils. The characteristics of ISEs made them advantageous over other techniques in the field of analysis of minerals, ores and soil samples. The ISEs may be used for determination of activity of a particular ion in wide concentration range (1×10^{-1} mol dm⁻³ to 1×10^{-6} mol dm⁻³) with some modifications in the technique of measurement. The lower detection limit could be brought down further.

For the analysis of naturally occurring minerals, ores and soils, several novel ISEs have been fabricated and their characteristics have been studied. The general methods of preparation of these electrodes, techniques to study their characteristics have been included in this chapter. Further the methodology used in the present work for the analysis of minerals, ores and soil samples have been outlined. In order to compare the values obtained by ISE techniques, other physico-chemical techniques such as atomic absorption spectroscopy, X-ray fluorescence, X-rays have been also used. A brief resume about these techniques has been also presented in this chapter.

Table: 2.1**Collection of Minerals**

S.No.	Minerals of Aluminium		Collection Sites
1	Bauxite A	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Gujrat
2	Bauxite B	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Madhya Pradesh
3	Bauxite C	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Bihar
4	Marl		Gujrat
5	Laterite		Gujrat
6	Clay		Gujrat
7	Basalt		Gujrat
	Minerals of Lead		
8	Galena	PbS	Gujrat
	Minerals of Magnesium		
9	Magnesite	MgCO_3	Tamil Nadu
10	Dolomite A	$\text{MgCO}_3 \cdot \text{CaCO}_3$	Rajasthan
11	Dolomite B	$\text{MgCO}_3 \cdot \text{CaCO}_3$	Tamil Nadu
12	Dolomite C	$\text{MgCO}_3 \cdot \text{CaCO}_3$	Tamil Nadu
	Minerals of Calcium		
13	Limestone	CaCO_3	Satna
14	Calcite	CaCO_3	Rajasthan
15	Chalk	CaCO_3	Rajasthan
	Minerals of Manganese		
16	Manganite	$\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Madhya Pradesh
	Minerals of Copper		
17	Copper Pyrite	CuFeS_2	Bihar
	Minerals of Zinc		
18	Zinc blende	ZnS	Gujrat
19	Calamine	ZnCO_3	Rajasthan
	Minerals of Iron		
20	Haematite	$\text{Fe}_2\text{O}_3 \cdot \text{nH}_2\text{O}$	Bihar
21	Clay Iron Stone		Maharashtra

2.2 COLLECTION OF SAMPLES

A number of naturally occurring minerals and soils were studied in the present work. These samples were collected from the different parts in India as shown in Fig. 2.1. The name of minerals with their formula and location are given in Table-2.1. Various soil samples also collected for this work from the different parts in India are given in Table-2.2 and Fig. 2.1.

Table: 2.2

Collection of Soil Samples

S.No.	Soil Samples	Collection Sites
1.	S ₁	Karbala (Allahabad)
2.	S ₂	Taj Mahal (Agra)
3.	S ₃	Botany Garden (Allahabad)
4.	S ₄	Ghorawal (Sonbhadra)
5.	S ₅	Panchgani (Satara)
6.	S ₆	Panchmarhi (Houshangabad)

2.2.1 Soil Samples

The collecting of samples were done using the method given in the literature. (1-5). The land were duck up to 15 cm and soil was taken out from different depths and were mixed together for making it homogeneous. The collected soil was brought to the laboratory and allowed to dry in the shade. Loose stubble, attached grasses and bigger stony particles were first removed then the soil samples were air dried on sheets of oilcloth. The air-dried soils were powdered in an agate mortar. The powdered soil samples were first sieved through a 100-mesh sieve (B.S.S. standard) and then kept in Winchester's bottles for the experiment.

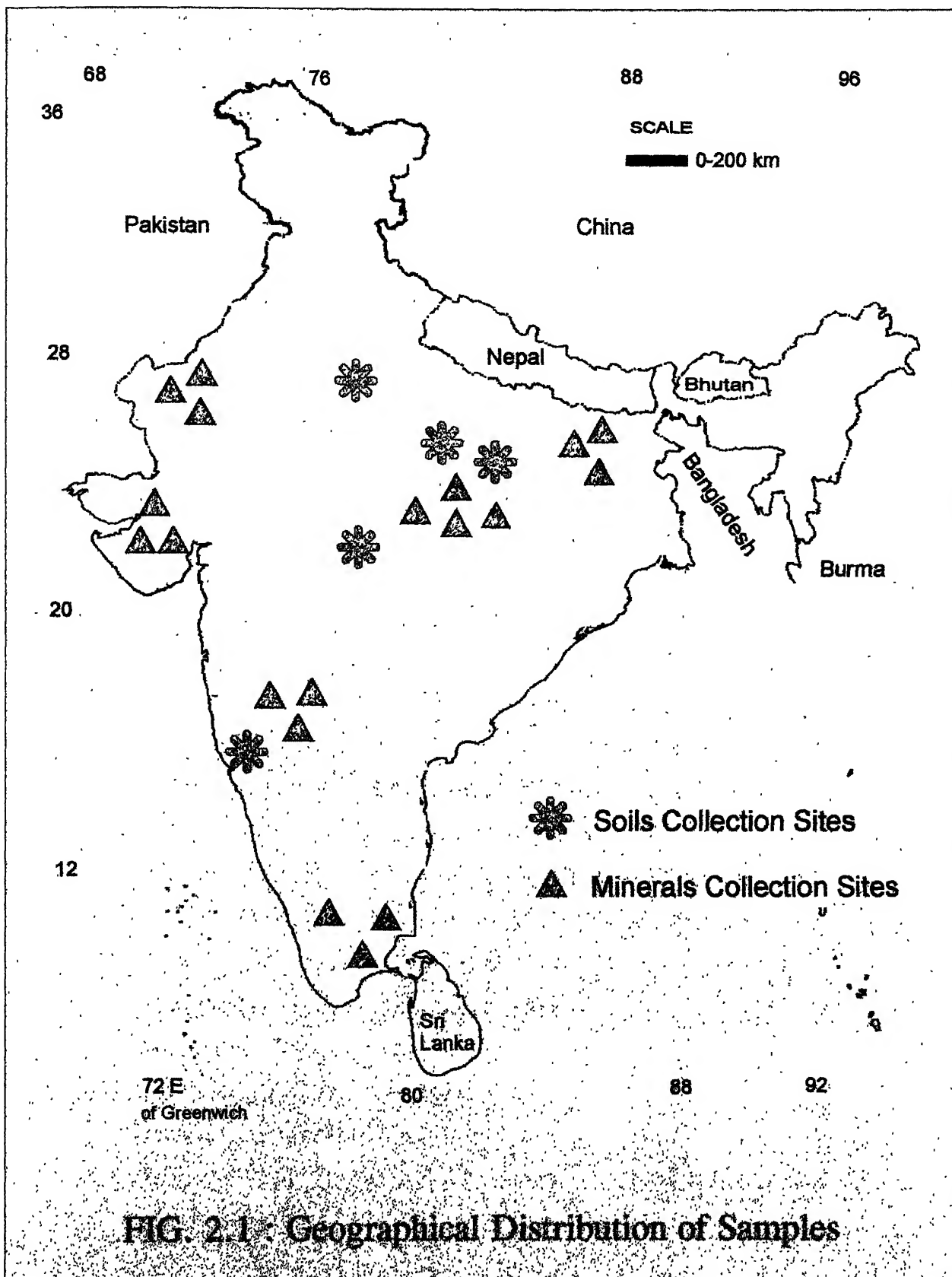


FIG. 2.1 : Geographical Distribution of Samples

2.2.2 Naturally Occurring Minerals and Ores

The sampling of ores and other minerals is a matter of great importance, since their market value is based on the results of the analyses of small samples. A general outline of the procedure is as follows

- 1) A large representative sample is obtained. Any "selection" of pieces different from the average in quality is avoided by taking portions according to some rigid system.
- 2) The large sample is then ground to a coarse powder and thoroughly mixed, and portions of this are again taken systematically, and the process of reduction in size and quantity repeated until a sample of small enough to be sent for analysis is obtained.

If the material was hard, it was first broken into coarse powder on a hard steel plate about (10 cm square and 4cm thick) with a hardened hammer. Loss of flying fragments was prevented by means of a steel ring (8 cm in diameter and 2.5 cm high) which was laid on the steel plate or in some other manner. The selected lumps one piece at a time, were placed in the cylinder (which fits into a depression in the block) and are crushed by striking the pestle with a hammer three or four times. The crushed material was transferred to a 100-mesh sieve, and sieved. The material that fails to pass the sieve was returned to the mortar for further crushing. This treatment was continued until the whole of the sample will pass a 100-mesh sieve.

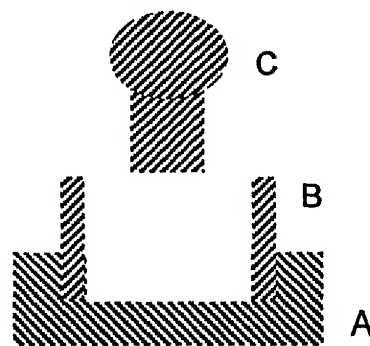


FIG. 2.2 : Percussion mortar

A "percussion mortar" (Fig.2.2) was used for crushing small lumps. The mortar consists of three pieces, a block (A), a hallow cylinder (B) and a pestle (C) all of very hard steel.

2.3 GENERAL METHOD OF PREPARATION OF ION SELECTIVE ELECTRODE

- (1) 50 g weight by weight of electroactive material and inert binder were homogeneously mixed on a filter paper (Whatman No. 42).
- (2) The paste was uniformly spread and was allowed to dry in air for one or two days to form a master membrane of about 0.5 mm in thickness.
- (3) The adhering filter paper was peeled off the next day.
- (4) A membrane disc of 1cm diameter was cut from the master membrane.
- (5) Both the membranes were kept immersed in 1.0 mol dm^{-3} solution of the metal ion for 48 hrs.
- (6) After this any portion of the filter paper still adhering to the surface of the membrane was removed and was dried in air.
- (7) The membrane was fixed to one end of a glass tube (diameter 1 cm., length 15 cm) with araldite and dried for 24 hrs.
- (8) The tube was filled with 0.1 mol dm^{-3} of metal ion solution for which the electrode was developed and was kept immersed in 0.01 mol dm^{-3} of same metal ion for seven days.
- (9) A saturated calomel electrode was inserted in the tube through the open end for contact with the internal solution, which served the purpose of internal reference electrode.

(Fig.2.3)

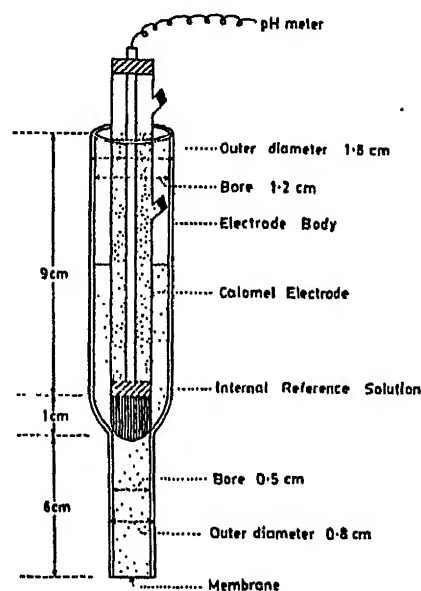


FIG. 2.3 : Diagrammatic sketch of membrane electrode

2.3.1 Instruments

A Philips pH-meter (Model PR 9405 m) with a saturated KCl calomel electrode was used for potential measurements. Silver-silver chloride electrode was also used as reference electrode.

A digital pH meter (Century CP 901) with electrodes was used for pH measurements. All the physicochemical measurements were performed at room temperature of $25 \pm 2^\circ\text{C}$.

2.3.2 Ionic strength

In every case, a constant ionic strength of 0.1 was maintained by using a solution of NaClO_4 or KCl , especially for potentiometric titration.

2.3.3 Characteristics of Electrodes

2.3.3.1 Linear Response

The linear response of all the different prepared ISEs was tested at different concentrations of the metal solutions. Solutions of various concentrations were prepared in each case and the corresponding potentials were measured. A curve was plotted between potential and metal ion concentration. The curve furnishes information on the lower detection limit and slope were determined to know the change of potential per decade change in concentration of particular ion (10).

2.3.3.2 Response Time

To determine the response time of the electrodes, the electrode was first dipped in 0.1 mol dm^{-3} solution of the relevant metal ion. The electrode is then taken out and immediately dipped in 0.01 mol dm^{-3} solution of the same metal ion and the value of potential was noted at 5 seconds interval. The period required to attain a steady potential was read from the plot.

2.3.3.3 Effect of pH

pH plays an important role in the performance of an ISE, hence, it is necessary to study the effect of pH on electrode response. Various set of solutions were prepared with a constant metal ion concentration of $1 \times 10^{-2} \text{ mol dm}^{-3}$ and the pH was varied from 1 to 10 by adding appropriate amounts of dil. HCl or dil. NaOH and the pH of each solution was measured. The electrode potential of each solution was also measured and subsequently a plot was made between pH and potential. The working pH range represented the limits in which the potential remained constant.

2.3.3.4 Interference due to other Cations

Selectivity coefficient is the basic source of information on the interference in ISE response. There are several experimental methods for the determination of selectivity coefficients. The numerical values determined depend to a certain degree on the method employed, this should always be specified. It has been pointed out (11) that these requirements are unfortunately often not met in the literature.

The experimental methods for determination of selectivity coefficient can be classified into two groups, namely, those involving the measurement of the electrode response in separate solutions, one containing the primary ion (i) and the other an interfering ion (j), and those measuring the electrode potential in solutions containing a mixture of the two ions. The first approach has been criticized (12), because it does not correspond to the real situation in analysis. This criticism is certainly justified; nevertheless, the values determined by the separate solution methods often agree reasonably well with those obtained by the mixed solution methods (12)

In present work the mixed solution method was used. In the mixed solution method (13,14), the electrode potential is measured in a series of a solution containing various activities of the primary ion and the constant activity of the interfering ion. In the E vs. pa_x plot (Fig.2.4), the "critical" activity a_i is found at the intercept of the extrapolated linear branches; activity a_i and the known activity a_j then determine the K_j^{pot} pot value according to equation (1)

$$K_j^{\text{pot}} = \frac{a_i}{a_j} \quad \dots (1)$$

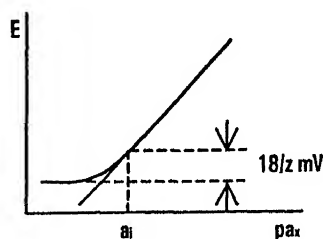


FIG. 2.4 : Determination of K_j^{pot} in mixed solution with constant activity of the interfering ion.

For determination of selectivity coefficients a series of solutions were prepared in which the concentration of the interfering ion was kept constant ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and the concentration of primary ion varied from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$. The potentials for each solution were noted and plotted against concentration on a semi-log graph paper. The selectivity coefficients were then calculated from the graph.

2.3.3.5. Life Time

After the fabrication of electrodes, usually get stabilized in one week time when the electrode give constant response and slope. After this period, it is necessary to check the electrode response every week to find out the lifetime of electrode through which the electrode response remains constant. The period through which the electrode response remains constant can be called the lifetime of the electrode. After this lifetime, the electrode gives erratic behaviour so it should not be used for any measurements.

2.3.3.6 Applications

(A) Potentiometric Titration

Potentiometric titration using ISEs as indicator electrodes greatly increases the precision of both precipitation and complexometric determinations. Since in potentiometric titration the operative parameter is the change in e.m.f. rather than the absolute value, the influence of liquid function potentials and activity coefficients is generally insignificant. Another advantage of this method compared with direct potentiometry is that the ion

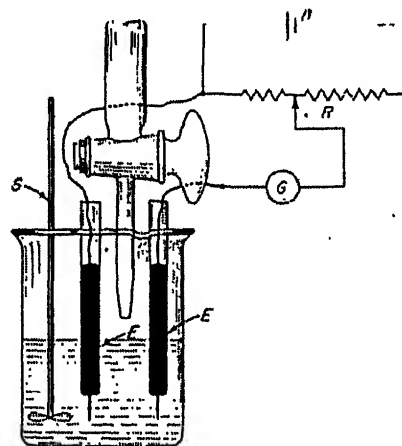


FIG. 2.5 : Potentiometric titration apparatus. B, dry cell; R, variable; G, galvanometer; E, E, electrodes; S, stirrer.

selective electrode may also be used to determine an ion for which the electrode is not selective by titrating with a solution of the ion for which the electrode is selective. (Fig. 2.5)

(B) Analysis of Minerals

Using ISEs different naturally occurring minerals and soil samples also analysed.

(C) Analysis of Soils

2.4 PREPARATION OF THE SAMPLE SOLUTION FOR THE MEASUREMENTS

The measurement can be performed only on a suitable solution. If the sample is not sufficiently soluble in water (or possibly in some other polar medium) such as soils, ores and naturally occurring minerals, it must be decomposed, the decomposition procedure must be chosen individually depending on the character of the material and the species to be determined. The chief requirements for the decomposition procedure are:

- a) the species to be determined must be quantitatively transferred into the solution,
- b) the amounts of interfering substances and reagents transferred into the solution must be as low as possible,
- c) the procedure should be simple and rapid.

The decomposition techniques available fall into several groups:

1. Decomposition with mineral acids
2. Fusion
3. Sintering
4. Leaching or extraction
5. Distillation
6. Mineralization
7. Sorption and absorption

2.4.1 Minerals and Ore Solution

The first three groups find use especially in the decomposition of mineral raw materials (15). Dilute or concentrated hydrochloric, nitric, perchloric and sulphuric acids are mostly used for the decomposition of minerals and ores in the present work, sometimes along with hydrofluoric acid when silicates are to be decomposed. Decomposition with acids is especially suitable for determination with cation selective electrodes as well as atomic absorption spectroscopy techniques.

2.4.2 Soil Extract

1.0 g soil was placed in 100 ml beaker. To this 10 ml of acid mixture of nitric acid, sulphuric acid and perchloric acid in (9:4:1) were added and the content of the flask was mixed by swirling. The flask was placed on low heat hot- plate. Then the flask was heated at higher temperature until the production of red NO₂ fumes ceases. The content were further evaporated until the volume was reduced to about 3 to 5 ml but not to dryness. The completion of digestion was confirmed when the liquid became colourless (16).

It was filtered in 100 ml volumetric flask and was made up to mark with the distilled water. The extract was properly preserved and used for different determinations.

2.5 CHEMICAL ANALYSIS

Under soil analysis the following characteristics were studied by using Atomic Absorption Spectroscopy and "Ion Selective Electrode" techniques. Method described by Jackson (16), was employed for the complete soil analysis.

The following parameters were determined:

1. Soil pH
2. potassium (K) contents
3. Magnesium (Mg)contents
4. Calcium (Ca) contents

5. Aluminium (Al) contents
6. Zinc (Zn) contents
7. Manganese (Mn) contents
8. Copper (Cu) contents
9. Lead (Pb) contents
10. Iron (Fe) contents

In the case of naturally occurring minerals the above mentioned cations were studied by ISE technique as well as XRF and AAS techniques.

2.5.1 Soil pH

A pH- meter (Century CP 901) measured the pH. The glass and calomel electrodes were immersed first into the buffer solution at varying pH for the standardization of the instrument. Then it was immersed into the test solution to record the pH of the test solution.

2.5.2 Analysis of Cations

The above mentioned cations K (I), Mg (II), Ca (II), Pb (II), Mn (II), Zn (II), Cu (II) and Fe (II) were studied by ISE method as well as atomic absorption technique. For this the samples were converted into solution form by using the above described method.

2.6 VERIFICATION OF RESULTS BY OTHER TECHNIQUES

As stated earlier nine different cations have been determined in different samples by ISE technique. It was also found necessary to verify these results by other standard techniques and for this purpose following techniques was employed.

2.6.1 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy can be used to advantage for the analysis of complex systems. The method is very specific, thus usually making any preliminary separation unnecessary. Atoms present in the ground state in the vapour phase can absorb the radiation of the wavelength corresponding to their resonant line. In

order to produce light of the wavelength corresponding to the resonant line of the metal, so called "hollow-cathode lamps" are used. The solution containing metal ions is sprayed into a flame, which is placed within the path of a light beam of constant intensity. The atoms formed in the flame absorb part of the radiation. The intensity of the light leaving the flame, I is

$$I = I_0 e^{-k'cl} \quad \dots(2)$$

Where,

I_0 is intensity of light before reaching the cell

c is concentration of absorbing atoms

k' is absorption coefficient at the wavelength used

l is path length

$$\text{Log } I_0/I = k'cl = \text{absorbance} \quad \dots(3)$$

i.e. the absorbance at a given wavelength is proportional to the concentrations of the absorbing atoms. On the basis of measuring absorbance using solutions of known concentrations a calibration curve can be obtained and the sample concentration can be determined after measuring the absorbance under the same conditions by means of the calibration diagrams.

2.6.2 X-Ray Fluorescence

Fluorescence occurs if an atom or molecule is excited by a photon and it re-emits part of its energy in the form of a radiation, while it returns to the ground state. The duration of the excited state is about 10^{-7} second and the phenomenon is termed as fluorescence.

Analytical procedures based on the phenomenon of fluorescence are termed fluorimetry. The condition of the fluorimetric determination of metal ions is that, it should be possible to convert the metal with an appropriate complex-forming agent into a chelate complex capable to show fluorescence.

The wavelength range of the absorbed radiation may range from visible light to X-rays. Absorption of visible and ultraviolet light brings about changes in the electron state of the molecules. When plotting the intensity of the fluorescent light, emitted by the excited molecule against the wavelength of the exciting light, a fluorescence spectrum-characteristic of the quality of the molecule is obtained. The intensity of fluorescent light is, in the proper concentration range (generally up to $10 \mu\text{g}/\text{cm}^3$) proportional to the concentration of the substance emitting fluorescent light.

The general arrangement of exciting dispersing and detecting fluorescent radiation with a plane-crystal spectrometer is shown diagrammatically in (Fig. 2.6). The specimen in the sampler holder is irradiated with an unfiltered beam of primary X-rays, which causes the elements present to emit their characteristic fluorescence lines. The entrance slit of the goniometer and directed into the plane surface of the analyzing crystal collimates a portion of the scattered fluorescence. The line radiations, reflected according to the Bragg condition, pass through an auxiliary collimator (exit slit) to the detector, where the energy of the X-ray quanta is converted into electrical impulses or counts.

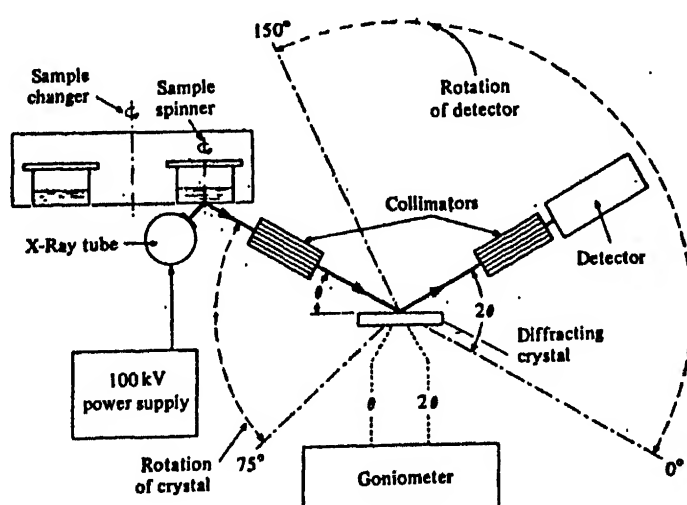


FIG. 2.6 : Geometry of a plane-crystal X-ray fluorescence spectrometer

2.6.3 X-Ray Diffraction

In order to characterise the zeolite prepared the x-ray studies on the synthetic zeolite was carried out which is described in chapter 3. The brief out line in the x-ray technique has been given in the following paragraphs.

X-ray diffraction techniques can be used for the examination of crystalline substances. Part of the radiation incident upon the crystal is scattered by the crystal lattice. The scattered radiation can be well observed only in directions in which the beams reflected from crystal planes under each other are amplified by interference. The condition of interference is according to Bragg, the following (Fig 2.7). If a monochromatic parallel beam of λ wavelength is incident upon a stationary crystal of the interplanar spacing (lattice constant) d at an angle θ , it will be reflected from each of the crystal planes under each other. The reflected rays either quench or attenuate, or else they amplify each other by interference. In accordance with the generally known laws of interference, amplification occurs of the difference in the distances of travel of the beams is an integral multiple of the wavelength.

The difference in the distance of travel of beams LMN and PQN is QM-QS. If S is the base point of the normal straight line projected from point M upon beam element P. If MR is the normal projected upon the lattice plane and d is the distance between the vicinal lattice planes in this directions, the difference in the distances of travel will- since $QM=QR$ -be $QM-QS=MR \sin \theta=2d \sin \theta$.

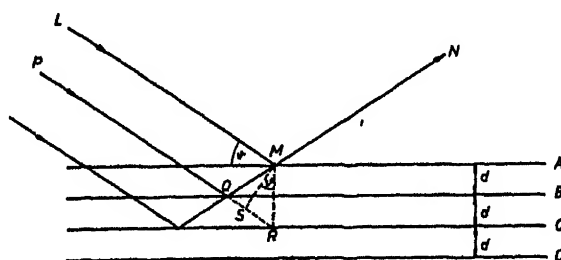


FIG. 2.7 : X-Ray reflections from crystals.

Interference occurs if the difference in distance of travel is an integral multiple of the wavelength, and so we may write.

$$n\lambda = 2d \sin \theta \text{ (Bragg's equation)}$$

Bragg's equation can be made use of from two points of views:

- (a) if the wavelength of the incident X-ray beam is known, the distance between neighboring lattice planes can be calculated;
- (b) if, on the other hand, the interplanar spacing is known, the wavelength of the radiation can be calculated. According to Bragg's equation is of fundamental importance in crystal structure research.

From the analytical point of view, powder diffraction techniques are the most significant of the X-ray diffraction techniques. The synthetic zeolite, willhendersonite was examined by the powder diffraction technique.

The fine powder of the sample was tested, among the help of crystal grains in total disorder, there was always be a sufficient number in such a position that the X-ray beam is incident on one or other of their lattice planes at the angle of θ as defined by Bragg's equation. These crystal grains cause reflection. Reflection occurs in any one of the planes that can be placed across the primary beam at an equal probability and accordingly the reflected beams proceed along the generatrices of cones whose half cone angle is equal to 2θ . This is shown in (Fig. 2.7 and 2.8).

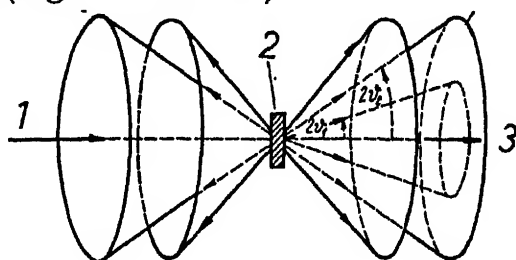


FIG. 2.8 : Diffraction of X-rays on a powder sample
1. incident beam 2. powder sample 3. emergent beam

2.6.4 Hydrothermal Technique

For the synthesis of zeolite the apparatus hydrothermal was used. The hydrothermal unit (Model HR-IB-2) manufactured by Tem-Pres Division, Leco Corporation, Pennsylvania, USA was used to carry out the experimental investigations.

This equipment can be run by 120/240 volt A.C., single-phase power source. Each furnace requires approximately 1000 watts. This equipment can be used for the studies up to 5 kb pressure and 1000°C. Fig. 2.9 show various components of the hydrothermal equipment.

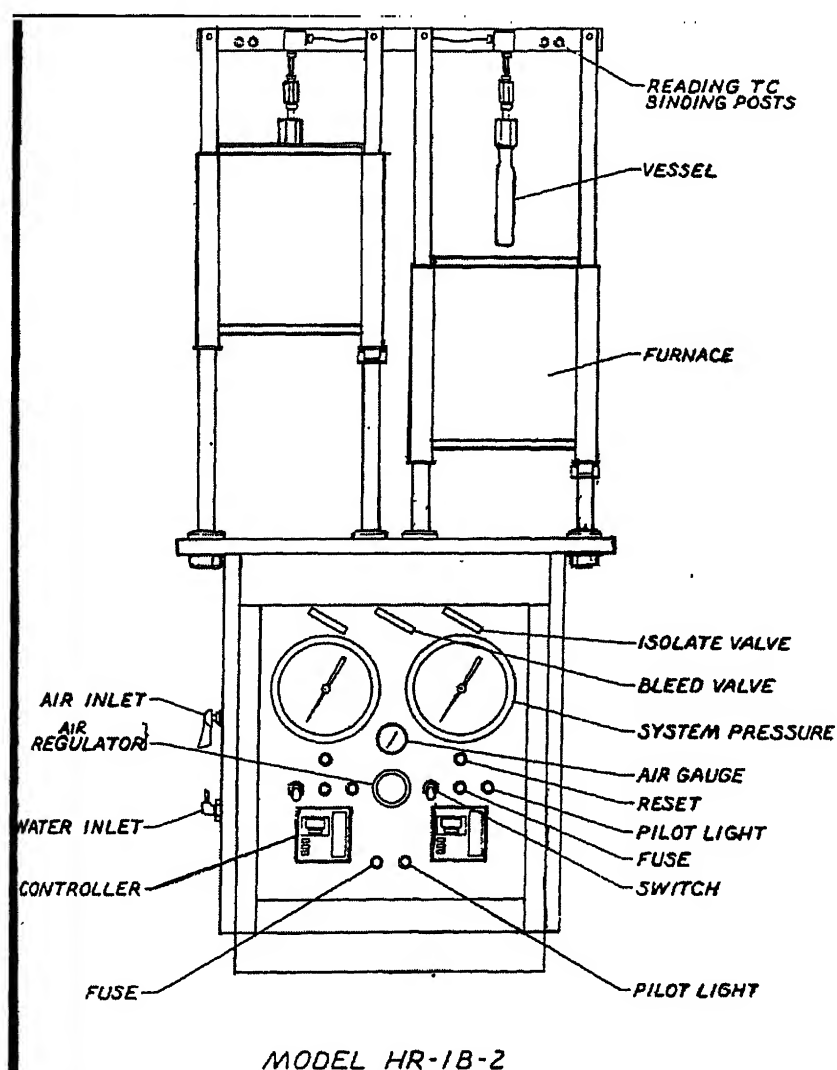


FIG. 2.9 : Schematic diagram of hydrothermal

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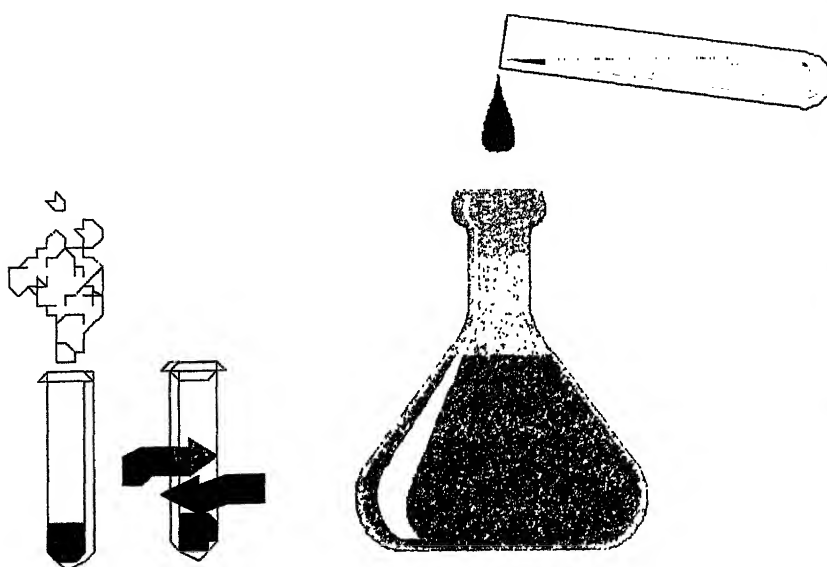
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CHAPTER 3

Synthesis of Zeolite and Electroactive Materials



SYNTHESIS OF ZEOLITE AND ELECTROACTIVE MATERIALS

3.1 INTRODUCTORY

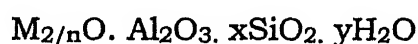
The present chapter deals with synthetic aspect of studies. In the section, which follows immediately, an introductory on zeolites has been presented, followed by the experimental work done in synthesized and characterising the zeolite.

In the subsequent section the synthesis for various metals of various electroactive materials have been included. These electroactive materials were subsequently being used for development of new ISEs for various metals.

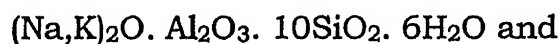
Zeolites are ubiquitous constituents in the vugs and cavities of basalts and other traprock formations. Beautiful assemblages of well-formed crystals up to several inches in size are prized by mineral collectors and adorn the mineral museum of every country. Several dozen individual species have been identified among which are chabazite, erionite, faujasite, and mordenite whose adsorption properties rival those of several synthetic molecular sieves.

Freihers Axel Fredrick Cronstedt, a Swedish mineralogist, discovered zeolites in 1756. Zeolites constitute one of the largest groups of minerals known, more than 40 distinct species have been recognized, and nearly 100 species having no natural counterparts have been synthesized in the laboratory. The potential application of both synthetic and natural zeolites stems, of course, from their fundamental chemical and physical properties, which in turn are directly related to their chemical compositions and crystal structures.

Along with quartz and feldspar minerals, zeolites are tektosilicates, that is they consist of three-dimensional frame works of SiO_4^{-4} tetrahedra where in all four-corner oxygen ions each tetrahedra are shared with adjacent tetrahedra. This arrangement of silicate tetrahedra reduces the overall Si:O ratio to 2:1, and if each tetrahedron in the frame work contains silicon as the silicon cation, the structure is electrically neutral, as is quartz (SiO_2). In zeolite structures, however, some of the quadrivalent silicon is replaced by trivalent aluminium, giving rise to a deficiency of positive charge. The charge is balanced by the presence of mono and divalent cations such as Na^+ , Ca^{2+} , K^+ etc., elsewhere in the structure. Thus, the empirical formula of a zeolite of the type:



Where, M is an alkali or alkaline earth cation, n is the valence of that cation, x is a number from 2 to about 10, and y is a number from 2 to 7. The oxide and unit-cell formulae of clinoptilolite, a common natural zeolite, follows:



Ions within the first set of parentheses in the unit-cell formula are known as exchangeable cations, those within the second set of parentheses are called structural cations, because with oxygen they make up the tetrahedral frame work of the structure. It should be noted that the base to alumina ratio is always equal to unity, and the (Al + Si) : O ratio is always 1:2. In addition, no zeolites are known which contain more tetrahedral aluminium ions than silicon ions, the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ is always equal to or greater than 2:1.

In 1909, Granjean demonstrated the adsorption properties of zeolites using chabazite and such gases as hydrogen, air, ammonia, H₂S and iodine, and in 1925, Weigel and Steinhoff noted that dehydrated zeolites would adsorb small organic molecules, but reject larger ones, a phenomenon described in 1932 by McBain as "molecular sieving". In the three decades that followed, dozens of papers on the synthetic zeolites and ion exchange properties of zeolite minerals appeared in the Chemical literature (1-9), mostly from the laboratories of R.M. Barrer in London and J. Sameshima in Japan. Much of this work was focused on the zeolites mordenite and chabazite which appeared to have the greatest adsorption capacities of the zeolites known at that time, however, the rarity of these zeolites, or of any zeolites for that matter, precluded the development of large-scale industrial processes based on natural materials. Zeolites were sufficiently abundant in amygdaloidal basalts for experimental purposes, but there seemed to be no method that could economically extract zeolites from such bodies to support a commercial process.

The non-existence of commercial deposits of natural zeolites caused the chemists to turn to synthesis as a means of obtaining a steady supply of zeolite materials, and between 1944 and 1960, major efforts went into the low-temperature hydrothermal synthesis of crystalline zeolites. Based on earlier experiments by Barrer, R.M. Milton of the Linde Division of Union Carbide Corporation began his own synthesis experiments in Tonawanda, New York. His initial runs, aimed at making chabazite because of its potential in the separation of oxygen and nitrogen from air, were unsuccessful. What was produced, however, was an entirely new type of zeolite, possessing adsorption and molecular sieve properties even better than those of cabazite. This new zeolite is the Linde type A zeolite (10, 11).

In 1914, Albert Johannsen found what he thought were fine-grained zeolites making up a large portion of Eocene tuff beds in the Uintah Basin of Utah, Colorado and Wyoming. In 1928, W.H. Bradley and C.S. Ross both described zeolites in saline-lake deposits of Wyoming and Arizona respectively, and in 1933, two U.S. Geological Survey geologists, M.N. Bramlette and E. Posnjak, reported several occurrences of clinoptilolite in vitric tuffs in various parts of the Western United States.

Thus, in the late 1950s, while the chemists were busy synthesizing zeolites, and finding uses for them, the geologists were realizing that many zeolite minerals could be found in minerable quantities in nature. The discovery that zeolite minerals were formed on a large scale by the reaction of volcanic tuffs and tuffaceous sedimentary rocks with lacustrine, marine, or ground waters in a host of geological environments was a milestone in the geological sciences. In less than three decades, the status of the zeolite group of minerals has changed from that of museum curiosity to an important industrial mineral commodity. The commercial use of natural and synthetic zeolites is still in its infancy, however, more than 300,000 tons of zeolitic tuff is currently mined each year in the United States, Japan, Italy, Bulgaria, Hungary, Germany, Korea and Mexico. Zeolites are used as filler in the paper industry, as light weight aggregate, in pozzolanic cements and concrete, as dietary supplements in animal husbandry, as ion exchangers in pollution-abatement processes and water purification, in the separation of oxygen and nitrogen from air, as reforming petroleum catalysts, in fertilizers and soil conditioners, and as acid resistant adsorbents in gas drying and purification.

3.2 SYNTHESIS OF WILLHENDERSONITE

Willhendersonite, ($\text{KCaAl}_3\text{Si}_3\text{O}_{12} \cdot 5\text{H}_2\text{O}$), (Potassium Calcium Aluminium Silicate Hydrate Zeolite) is a new zeolite, which is isostructural with chabazite ($\text{Ca Na}_2 [\text{Al}_2 \text{Si}_4\text{O}_{12}] 6\text{H}_2\text{O}$ (11). It occurs in the San Venanzo Quarry, Terni, Umbria, Italy in cavities of Quaternary lavas as “trellis like” twinned aggregates, and as tabular crystals in a limestone xenolith from the Ettringer Bellerberg near Mayen, Eifel Germany. Associated minerals include gismondine, chabazite, phillipsite, thomsonite, ettringite and thaumasite.

In present work an ascent was made to synthesize this zeolite and study it from the point of view of its composition. The experimental details are given below-

3.2.1 Preparation of Starting Materials

1 Potassium Carbonate (K_2CO_3)

As a source of K_2O (Sarabhai Chemicals)

2 Calcium Carbonate (CaCO_3)

As a source of CaO (Sarabhai Chemicals)

3 Silica (SiO_2)

The source of SiO_2 is pure quartz crystals collected from Deccan Traps, Matheran Maharashtra. This was uniformly crushed to about 60 mesh and then treated with hot hydrochloric acid followed by washing with distilled water and kept in the oven for drying.

4 Alumina (Al_2O_3)

Anhydrous extrapure, γ -alumina (Sarabhai Chemicals). It was dried in oven at 500°C before use.

3.2.2 Apparatus Used in Making Samples

1 Oven

It may be set at the desirable temperature up to 250°C. This was used to keep various starting materials free from moisture.

2 Single Pan Balance

This was used for the weighing purposes and can weigh with a precision of 0.00001 g up to 99.99999 g.

3 Silicon-Carbide Furnace

This furnace comprises four silicon-carbide rods (44 cm long, 1.5 cm diameter) as heating elements. The hot zone is 15 cm long and 1.5 cm in diameter. It can achieve maximum temperature up to 1250°C. This furnace was used for making potassium disilicate as it can run for longer duration.

4 Electric-Chamber Furnace (Model-70 C 5)

This was used for making sintered sample. It comprises five molybdenum disilicide elements with the furnace chamber specifications as 12.5 cm wide x 15.0 cm high x 25.0 cm deep. It can achieve temperature (max.) up to 1480°C. Its temperature can be controlled automatically for desired duration and at a fixed value with the help of Temprotect.

5 Hydrothermal

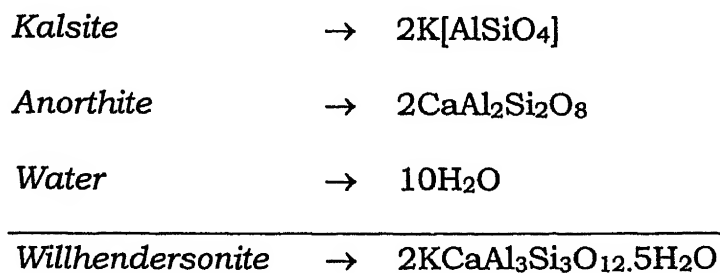
This apparatus was used in the synthesis of zeolite. The detail of this was given in chapter 2.

6 Platinum Crucible, Platinum Tubes and Platinum Wire

Used for making samples.

3.2.3 Method for Synthesis of Willhendersonite

Willhendersonite ($\text{KCaAl}_3\text{Si}_3\text{O}_{12}\cdot 5\text{H}_2\text{O}$) is mixture of *kalsite* (KAlSiO_4) and *anorthite* ($\text{CaAl}_2\text{Si}_2\text{O}_8$).



Therefore, for synthesis of *willhendersonite* first *kalsite* and *anorthite* was prepared.

3.2.3.1 Synthesis of Kalsite

Kalsite is a mixture of potassium disilicate ($\text{K}_2\text{O}\cdot 2\text{SiO}_2$) and alumina (Al_2O_3). First potassium disilicate was prepared.

Since potassium (all alkalies) volatilizes appreciably at high temperatures (13) therefore, instead of K_2CO_3 , $\text{K}_2\text{Si}_2\text{O}_5$ was used as a source of K_2O . The method followed for the preparation of $\text{K}_2\text{Si}_2\text{O}_5$ was that of Schairer and Bowen (14).

K_2CO_3 and SiO_2 were kept in oven at 60°C for 24 hours. These dry powdered chemicals were weighed in a platinum crucible in this required proportion and mixed with a spatula. This platinum crucible was then placed in the silicon-carbide furnace at 600°C and the crucible was heated for 3 hours at this temperature. The melted $\text{K}_2\text{Si}_2\text{O}_5$ was cooled in air and immediately placed in the dessicator. A colourless glass was obtained at this stage. Then the crucible was weighed which shows the alkali loss of the order of 10^{-2} g due to volatilization. To compensate the loss in weight, the required amount of K_2CO_3 was again added and the crucible was heated again at 1100°C for 45 minutes. This cycle was

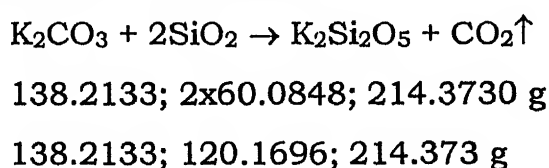
repeated till the loss of K₂O was compensated. The calculation for the preparation of K₂Si₂O₅ are given in Appendix-1

Appendix-1

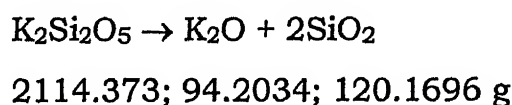
Calculations for the preparation of K₂Si₂O₅

Mol. wt. of K ₂ CO ₃	138.2133 g
Mol. wt. of K ₂ O	94.2034 g
Mol. wt. of SiO ₂	60.0848 g
Mol. wt. of K ₂ Si ₂ O ₅	214.3730 g

The reaction for the preparation of K₂Si₂O₅ is



Also, Chemical formula of K₂Si₂O₅ constitutes,



For 1.0 g of K₂Si₂O₅, the required amount of

$$\text{K}_2\text{O} = 94.2034 / 214.373 = 0.43944 \text{ g}$$

$$\text{SiO}_2 = 120.1696 / 214.373 = 0.56056 \text{ g}$$

$$\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2\uparrow$$

$$138.2133; 94.2034 \text{ g}$$

The source of K₂O component is K₂CO₃ and due to the loss of CO₂, the mass of K₂CO₃ required to give 1.0g of K₂O is,

$$138.2133 / 94.2034 = 1.4672 \text{ g}$$

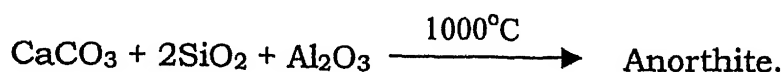
$$\text{So for 1.0 g of K}_2\text{Si}_2\text{O}_5 \text{ the required K}_2\text{CO}_3 = 1.4672 \times 0.4394$$

$$= 0.64474 \text{ g}$$

Thus after preparation of potassium disilicate was formed and then alumina (Al₂O₃) was added in this glass and *kalsite* was formed.

3.2.3.2 Synthesis of Anorthite

For the preparation of *anorthite*, the calcium disilicate was formed by using the same method as described above. Then the alumina was added in the calcium disilicate, and the *anorthite* was formed.



3.2.4 Synthesis of Sample ($\text{KCaAl}_3\text{Si}_3\text{O}_{12} \cdot 5 \text{H}_2\text{O}$)

Kalsite (KAlSiO_4) and *anorthite* ($\text{CaAl}_2\text{Si}_2\text{O}_8$) were mixed in appropriate proportions in agate mortar. Acetone was added during mixing of the chemicals. The mixture was ground thoroughly by a pestle for about one hour. The homogeneous mixture was dried in an oven and then it was transferred to a platinum crucible. A silicon carbide furnace was used for the fusion of the mixture at a temperature well above its liquids. The silicate melt was quenched in water. The glass was rushed to fine powder and measuring the R.I. of different grains checked its homogeneity. The R. I. for the glass was measured by the liquid immersion method. Now the sample was ready for experiments.

3.2.5 Capsule Preparation Technique

The platinum capsules were sealed with the help of a carbon-arc spot welder. Using a graphite (pencil form) electrode did this. Firstly, one end of the tube was sealed and then the distilled water was injected into the tube through a micro-syringe and the tube was weighed. The required amount of *willhendesonite* was then loaded into the tube and weighed again. The calculated amount of *willhendesonite* was added (depending upon the CO_2 and H_2O ratio) and the assembly was weighed again. The open end of the tube was then sealed. After the capsule is made, it was weighed to check any probable loss of volatile during

welding. The sealing is considered to be perfect if the weight of this capsule remained constant after putting it inside the oven for an hour.

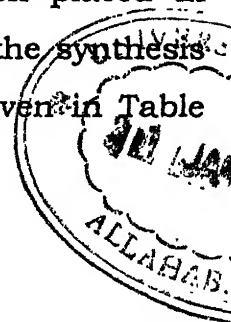
The five tubes were prepared and these tubes then placed in hydrothermal at different temperatures and pressures for the synthesis of *willhendersonite*. The details of these experiments are given in Table

3.1.

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4940

Table : 3.1

Synthesis of *willhendersonite*



Experiment Number	Pressure (Kb)	Temperature ($^{\circ}\text{C}$)	Run (days)	Remark
1	1	400	20	Willhendersonite formed
2	1	450	15	Willhendersonite formed
3	1	500	12	Willhendersonite formed
4	$\frac{1}{2}$	400	15	Willhendersonite formed
5	$\frac{1}{2}$	450	12	Willhendersonite formed

3.2.6 Characterization

3.2.6.1 X-Ray Crystallography

In order to characterise the sample, X-ray diffraction studies were done at I.I.T. Kanpur in the Material Science Department. The instrument used was ISO DEBYEFLEX (2002) (RICH SEIFERT). Single crystal precession photographs of crystals show that *willhendersonite* was triclinic, space group P1 or P1 with $a=9.23$ (2), $b=9.21$ (2), $C=9.52$ (2) \AA , $\alpha=92.7(1)$, $\beta=92.4(1)$, and $\gamma=90.1(1)^{\circ}$ with $Z=2$.

The X-ray analysis further showed that *willhendersonite* was isostructural of *chabazite* with complete Si-Al ordering as indicated by T-O distances, that is the tekto silicate frame works of both the minerals were similarly, and consist in part, of double six rings of tetrahedra, although the co-ordination of Ca were very different.

Powder X-ray diffraction data are listed in Table 3.2. They were obtained using a synthesized sample of *willhendersonite*, crystal fragments mounted in a Gadolfi camera (114.6 mm diameter) with silicon as an internal standard.

The X-ray data's shown that the **sample 3**, that is, *willhendersonite*, which was synthesized at *1Kb pressure, temperature at 500°C and running in 12 days* under hydrothermal was best prepared. The calculated d-values of all the synthesizing zeolite are similar to values of naturally occurring *willhendersonite* zeolite.

Table: 3.3
Microprobe Analysis of Willhendersonite

Sample taken	KCaAl ₃ Si ₃ O ₁₂ 5H ₂ O
	Wt. %
K ₂ O	8.59
CaO	10.65
Al ₂ O ₃	29.05
SiO ₂	34.26
H ₂ O	17.09
Total	100.00

3.2.6.2 Chemical Analysis of Willhendersonite

Willhendersonite was chemically analyzed utilizing an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and beam current of 0.15 µA at Material and Science Department in Kanpur IIT. The results of the analysis are also listed in Table 3.3.

The crystal structure analysis Tillmanns and Fischr (15, 16) confirm the ordering of Al and Si, and K and Ca which is implied by this formula. A difference Fourier synthesis suggests that there are one

potassium atom and five water molecules per formula unit. Thus the composition of *willhendersoinite* from both occurrences is very close to the ideal one, $\text{KCaSi}_3\text{Al}_3\text{O}_{12}\cdot 5\text{H}_2\text{O}$ for comparison, the formula of *chabazite* is $(\text{Ca}, \text{Na}_2) (\text{Al}_2\text{Si}_4\text{O}_{12})\cdot 6\text{H}_2\text{O}$.

Table: 3.2

X-Ray Powder Diffraction data for Zeolite. The d-Values were Calculated for all the 5 Samples and shown below

$d_{(obs.)}$	$d_{(calc.)}$ 1	$d_{(calc.)}$ 2	$d_{(calc.)}$ 3	$d_{(calc.)}$ 4	$d_{(calc.)}$ 5	Int.	h	k	l
9.160	9.000	9.100	9.150	9.130	9.110	100	1	0	0
5.180	5.000	5.100	5.180	5.000	5.110	30	1	1	1
4.710	4.100	4.700	4.720	4.700	4.650	5	0	0	2
4.570	4.110	4.500	4.580	4.600	4.590	5	2	0	0
4.270	4.000	4.300	4.270	4.300	4.190	2	1	0	2
4.090	3.900	4.000	4.090	4.010	4.010	40	2	1	0
4.090	3.900	4.010	4.100	4.000	4.000	40	1	2	0
3.930	3.800	3.900	3.930	3.890	3.900	20	1	1	2
3.820	3.800	3.810	3.840	3.790	3.800	20	1	2	1
3.710	3.700	3.700	3.730	3.600	3.700	30	2	1	1
3.710	3.700	3.710	3.700	3.610	3.710	30	1	1	2
3.060	3.000	3.070	3.060	3.000	3.010	10	2	1	2

3.060	3.000	3.060	3.050	3.010	3.020	10	3	0	0
3.010	3.000	3.000	3.020	3.000	3.000	10	0	1	3
3.010	3.000	3.020	3.000	3.010	2.960	10	1	2	2
2.907	2.900	2.900	2.900	2.915	2.901	60	1	1	3
2.804	2.800	2.801	2.809	2.814	2.789	50	1	3	1
2.746	2.700	2.747	2.747	2.716	2.719	2	2	2	2
2.746	2.701	2.751	2.747	2.700	2.740	2	1	3	1
2.674	2.601	2.670	2.670	2.600	2.670	1	2	2	2
2.538	2.510	2.530	2.541	2.510	2.501	20	2	0	3
2.538	2.500	2.535	2.539	2.500	2.505	20	2	3	0
2.508	2.501	2.500	2.511	2.501	2.502	20	0	3	2

3.3 SYNTHESIS OF ELECTROACTIVE MATERIALS

3.3.1 Potassium Tetraphenyl Boron

10 mg of potassium salt was dissolved in 50 ml of distilled water. The pH was adjusted 4-5 by adding dil HCl solution. The solution was heated 40-50°C and then 3% aqueous solution of sodium tetraphenyl boron was added. A white precipitate (17) was formed, which was filtered, washed and dried at room temperature over night. This precipitate was used as electroactive material for preparation of Pb(II) electrode.

3.3.2 Calcium Succinate

To neutral solution of CaCl₂ in distilled water gives precipitate with solution of succinic acid (B.D.H.) in water. Curdy white precipitate was formed which was filtered, washed and dried at room temperature over night. This *calcium succinate* was used as electroactive material for preparation of Ca(II) electrode.

3.3.3 Calcium Citrate

To neutral solution of calcium chloride distilled water gives white precipitate with solution of citric acid (B.D.H.) in distilled water. This precipitate was filtered, washed and dried at room temperature over night. This *calcium citrate* was used as electroactive material for preparation of Ca(II) electrode.

3.3.4 Magnesium p-dimethylaminoazobenzene Sulfonate

To the solution of sodium p-dimethylaminoazobenzene sulfonate (methyl orange) in distilled water was added in solution of magnesium chloride in water, orange crystals were formed (18-20). Which was filtered, washed and dried at room temperature over night. This precipitate was used as electroactive material for preparation of Mg (II) electrode.

3.3.5 Aluminium Diphenylamine

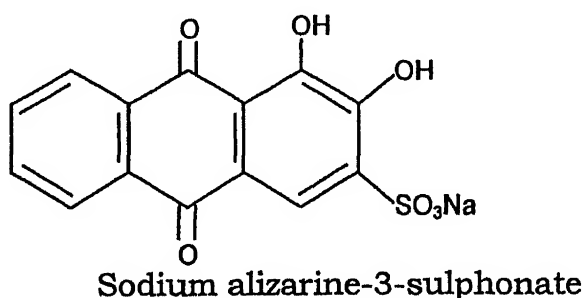
The solution of diphenylamine (B.D.H.) in alcohol when added to the solution of aluminium chloride a white precipitate was obtained (19). Which was filtered washed with distilled water and dried at room temperature over night. This *aluminium diphenylamine* was used as electroactive material for the preparation of Al (III) electrode.

3.3.6 Aluminium Benzoate

Solution of aluminium chloride in distilled water was added in the solution of benzoic acid (B.D.H.) in ethanol to get a white precipitate (22). Which was then filtered washed with distilled water and dried at room temperature over night. This *aluminium benzoate* was also used as electroactive material for the preparation of Al (III) electrode.

3.3.7 Aluminium Alizarine-3 Sulphonate

Aluminium salt gives red precipitate with alizarine sulphonic acid in an ammonical solution. For this 5 ml of neutral solution of aluminium chloride was added in 1 ml of 0.1 percent alizarine sulphonic acid (sodium salt) (B.D.H.) solution and then ammonium hydroxide was added until the mixture become alkaline. The solution was boiled for few minutes and cooled. The mixture was then acidifies with dil acetic acid, a red colour precipitate was formed (23). Which was filtered washed with distilled water and dried at room temperature over night. This precipitate was also used as electroactive maternal for Al (III) ISE.

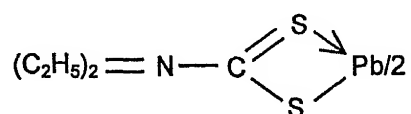


3.3.8 Lead Molybdate

0.1 g. of ammonium molybdate was dissolved in 200 ml of distilled water and 15 ml of 2N-HCl and 10 g. of ammonium acetate was added. This solution was heated to boiling and then 5 ml of lead acetate solution was added from a burette whilst stirring until no further precipitation take place. The white precipitate (24) was filtered, washed and dried at room temperature for over night. Now this precipitate was used as electroactive material for preparation of Pb(II) electrode.

3.3.9 Lead Diethyldithiocarbamate

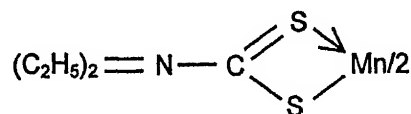
20% solution of sodium diethyldithiocarbamate (B.D.H.) in distilled water was added in the 10% solution of lead salt, white curdy precipitate (25) was formed. Which was filtered, washed and dried at room temperature over night. This precipitate was used as preparation of Pb(II) electrode .



Lead diethyldithiocarbamate

3.3.10 Manganese Diethyldithiocarbamate

To the 20% solution of sodium diethyldithiocarbamate (B.D.H.) in distilled water 10% solution of manganese salt, was added brown precipitate (25) was formed. Which was filtered, washed and dried at room temperature over night. This precipitate was used as preparation of Mn(II) electrode.



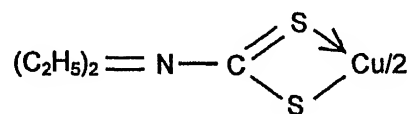
Manganese diethyldithiocarbamate

3.3.11 Iron Quinol

0.5 g of quinol (B.D.H.) was dissolved in alcohol. This solution was added drop wise in the 0.1M solution of ferric chloride in distilled water. A black precipitate was formed immediately. This precipitate was filtered, washed with distilled water and dried at room temperature over night. Now this precipitate was used as an electroactive material for the fabrication of Fe (III) electrode.

3.3.12 Copper Diethyldithiocarbamate

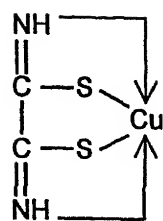
A brown precipitate of *copper diethyldithiocarbamate* (26) was formed when an aqueous solution of sodium diethyldithiocarbamate (B.D.H.) was added to a neutral solution of copper sulphate (B.D.H). This precipitate was filtered, washed and dried at room temperature over night. This precipitate was used as electroactive material for preparation of Cu(II) electrode.



Copper diethyldithiocarbamate

3.3.13 Copper Rubeanate

An alcoholic solution of rubeanic acid gives a black precipitate of *copper rubeanate* (27, 28) from an ammoniacal solution of copper salt. For this, 5 ml solution of rubeanic acid in alcohol, was added to the solution of copper salt, a black precipitate was formed. Which was filtered, washed and dried at room temperature over night. This copper *rubeanate* was used as an electroactive material for preparation of Cu (II) electrode.



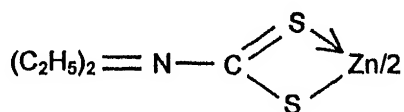
Copper rubeanate

3.3.14 Zinc Urate

5.0 g. of potassium hydroxide was dissolved in 100 ml of distilled water. This solution was added in 0.1M solution of zinc chloride until the precipitate zinc hydroxide re-dissolved. 2.0 g. of uric acid ($C_5H_4O_3N_4$) (B.D.H.) dissolved in 100ml of distilled water and this solution was added in above solution to form a gelatinous precipitate of *zinc urate* (29-31). The precipitate was greenish-blue in colour, filtered, washed with distilled water and dried at room temperature over night. This *zinc urate* precipitate was used as an electroactive material for preparation of Zn (II) electrode.

3.2.15 Zinc Diethyldithiocarbamate

To 10 ml solution of 10% zinc acetate in distilled water, 20% solution of sodium diethyldithiocarbamate was added until white curdy precipitate of *zinc diethyldithiocarbamate* (32,33) was formed. This precipitate was filtered, washed with distilled water and dried at room temperature over night. This *zinc diethyldithiocarbamate* was also used as an electroactive material for the preparation of Zn (II) electrode.



Zinc diethyldithiocarbamate

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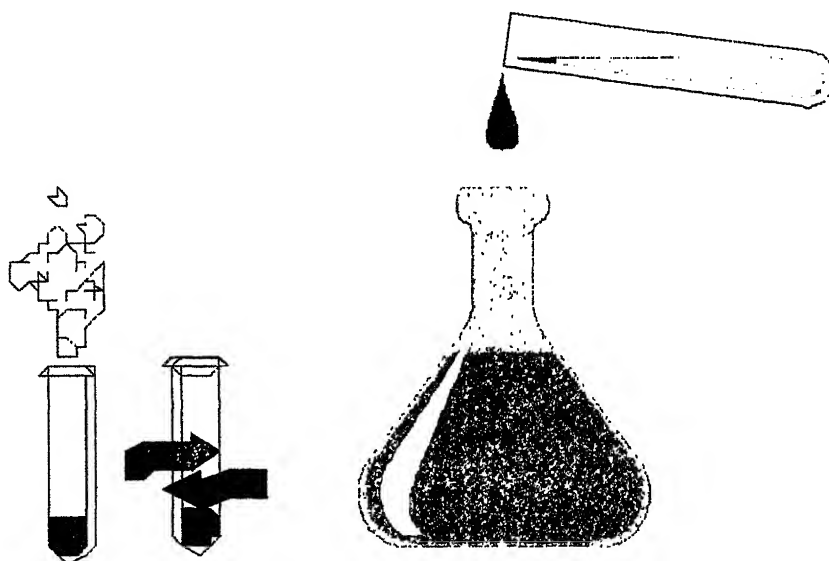
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CHAPTER 4

ISEs of K (I), Mg (II), Ca (II)
and their Applications in
Limestone, Calcite, Chalk, Dolomite,
Magnesite and Soils



ISEs OF K(I), Mg(II), Ca(II) AND THEIR APPLICATIONS

4.1 INTRODUCTORY

This chapter contains the method of fabrication as well as characteristics of new ion selective electrodes for K (I), Mg (II) and Ca (II) ions and their possible applications in the field of naturally occurring minerals such as *limestone, dolomite, chalk, calcite, magnesite* and *soil* samples.

4.2 POTASSIUM ION SELECTIVE ELECTRODE

The first K(I) ISE reported in the literature is the modified glass electrode which became popular for some times (1-3). There after potassium tetra-p-chlorophenyl borate was used an electroactive material for fabrication of PVC membrane electrode for K(I) ion (4,5). K(I) ISEs based on neutral ion carriers, specially valinomycin were found to have very high selectivity for potassium ion (6-11). The application of K(I) ISEs in clinical measurements (6,12,13,16) provided the necessary impetus to the development of K(I) ISEs.

The poly ethers synthesized by Pedersen (14) was also used for the fabrication of K(I) ISE. The potassium-dimethyl dibenzo-30-crown-10, based ISE in PVC matrix (15,16) have been fabricated. The K(I) ISE without internal reference solution have been also reported. The K(I)-ISFET (ion- sensitive field- effect transistor) electrode (17) were also developed. Simon and co-workers (18) have used potassium tetraphenyl borate in PVC matrix for fabrication of K(I) ISE.

In this work the *potassium tetraphenyl boron* was used as electroactive material but the matrix was changed to epoxy resin which does not need any plastisizer because it is reported that PVC electrode need plastisizers and plastisizers based electrodes create problem in certain measurements.

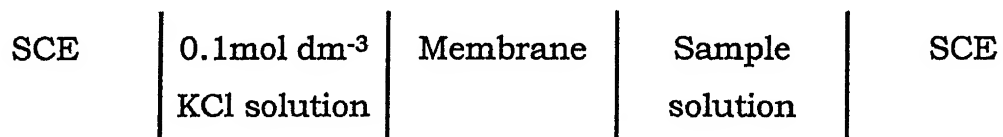
Using this electrode the potassium content of following naturally occurring minerals, *limestone, dolomite, chalk, calcite, magnesite* and *soil samples* were determined and compared the values obtained by other methods.

4.2.1 Preparation of Electrode

The electroactive material *potassium tetraphenylboron* was prepared as described in chapter 3. Then it was mixed with araldite in 1:4 ratio to prepare a master membrane as described in chapter 2. Care was taken that the membrane thickness was uniform and was 0.5mm. From master membrane a small portion was cut and plugged into a barrel shaped tube in which the reference solution was 0.1 mol dm^{-3} KCl and a saturated calomel electrode was inserted inside the electrode for electric contact.

4.2.2 Characteristics of Electrode

The ISE thus prepared was dipped in 0.01 mol dm^{-3} solution of K(I) ion for one week so that the measured potential gets stabilised. In order to make potential measurement the ISE was used as an indicator electrode and a second saturated calomel electrode was used as reference electrode. The whole assembly can be represented as-



A Philips pH-meter (PR 9405) was used for potential measurements, and a glass electrode was used for pH measurement. All the measurements were carried out at room temperature ($25 \pm 2^\circ$). The following characteristics of the electrode was studied.

4.2.2.1 Electrode Response

To determine the electrode response of K(I) ISE, a series of solutions of varying concentrations from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ of K(I) ions were prepared. The electrode potential of each solution was recorded (Table 4.1) and the concentration of ion was plotted against the electrode potential on a semilog graph paper (Fig.

4.1). From the graph it was observed that the potentials became constant after a certain lowering of concentration of K(I) ion. The graph shows that the linear response was down to K(I) concentration $1 \times 10^{-4} \text{ mol dm}^{-3}$ with 30 mV per-decade change in K(I) ion concentration.

4.2.2.2 Response Time

The electrode was first dipped in 0.1 mol dm^{-3} solution of K(I) ion and potential was noted. The electrode was immediately shifted to 0.01 mol dm^{-3} solution and the potentials were noted at 5 seconds interval (Table 4.2). These potentials were plotted against time (Fig. 4.2) and it was found that after 20 seconds the electrode attained a constant potential. The time taken by the electrode to reach a constant potential was 20 seconds.

4.2.2.3 Effect of pH

For this a series of solutions of varying pH 1 to 12 were prepared keeping the concentration of the K(I) ion constant 0.01 mol dm^{-3} . The potentials of all the solutions were recorded (Table 4.3) and plotted against corresponding pH (Fig. 4.3). It was found that from pH range 3 to 11 the electrode potentials remains constant. Therefore the working pH range of electrode is 3 to 11.

4.2.2.4 Selectivity Coefficient

The selectivity coefficient of the electrode was determined by mixed solution method. For this a series of solutions of K(I) ion were prepared, in which the concentration of interfering ion was kept constant ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and the concentration of K(I) ion was varied from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$. The potential for each solution was noted and plotted against concentration of K(I) ion on a semilog graph paper (Fig. 4.1). It was found that the following ions do not interfere : Na(I), Ca(II), Mg(II), Ba(II), Pb(II), Al(III), Zn (II), Cu(II).

Table : 4.1**Electrode Response**

Concentration of metal ion (mol dm ⁻³)	Electrode Potential(mV)	
	K(I)ISE	Mg (II) ISE
1x10 ⁻¹	262	195
5x10 ⁻²	250	186
1x10 ⁻²	215	169
5x10 ⁻³	200	154
1x10 ⁻³	175	130
5x10 ⁻⁴	164	111
1x10 ⁻⁴	135	85
5x10 ⁻⁵	135	75
1x10 ⁻⁵	135	62
5x10 ⁻⁶	135	55
1x10 ⁻⁶	135	55
5x10 ⁻⁷	135	55

Table : 4.2**Response Time**

Time (Sec)	Electrode Potential (mV)	
	K(I) ISE	Mg(II) ISE
0	262	195
5	252	190
10	242	185
15	230	180
20	222	169
25	222	169
30	222	169
35	222	169
40	222	169

Table : 4.3**Effect of pH**

pH	Electrode Potential (mV)	
	K(I)ISE	Mg(II) ISE
1.0	262	197
2.0	228	165
3.0	215	165
4.0	215	165
5.0	215	165
6.0	215	165
7.0	215	165
8.0	215	165
9.0	215	165
10.0	215	175
11.0	212	—
12.0	225	—

Table : 4.4**Selectivity Coefficient**

Ions	$K_{K^+,M}^{pot}$	$K_{Mg^{2+},M}^{pot}$
Na(I)	0.200	—
Ca(II)	0.006	0.04
Mg(II)	0.006	—
Ba(II)	0.006	0.04
Pb(II)	0.003	0.04
Al(III)	0.000	0.00
Zn(II)	0.003	0.10
Cu(II)	0.003	0.10
Ni (II)	—	0.10
Fe (III)	—	0.00

FIG. 4.1 : Potential vs $-\log$ Concentration of $K(I)$ Ion
in Presence and Absence of Secondary Ions

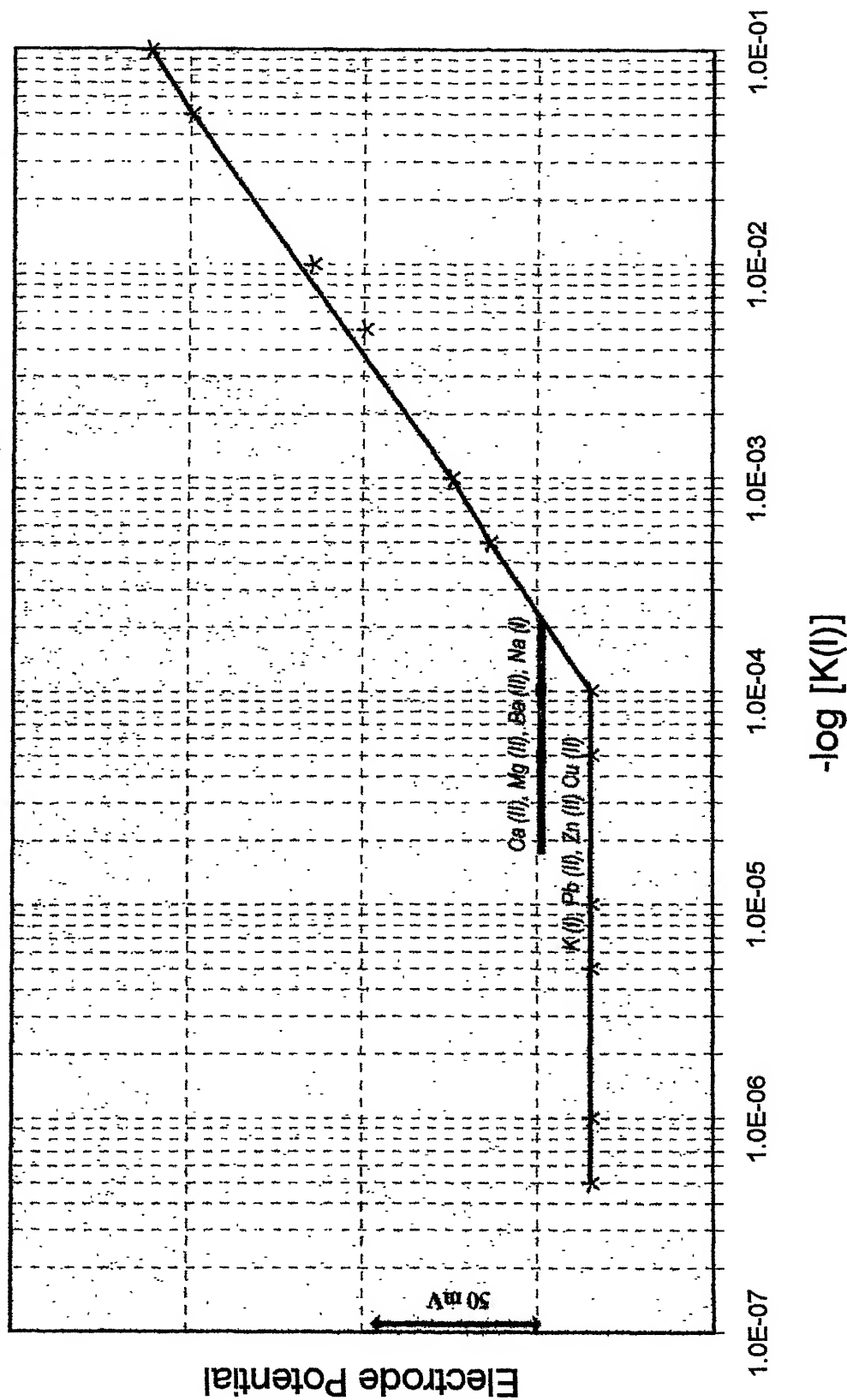


FIG. 4.2 : Potential vs. Time

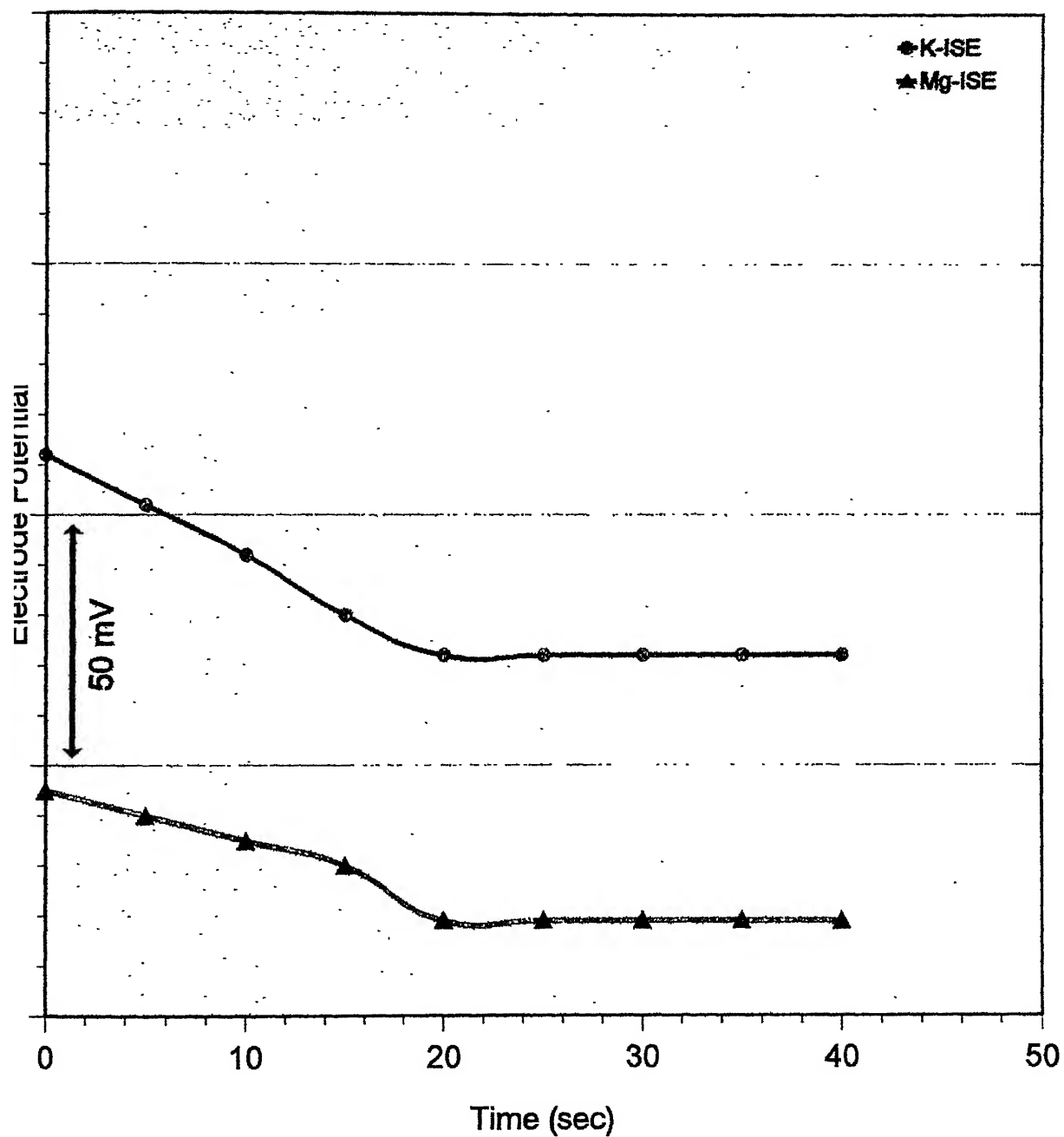
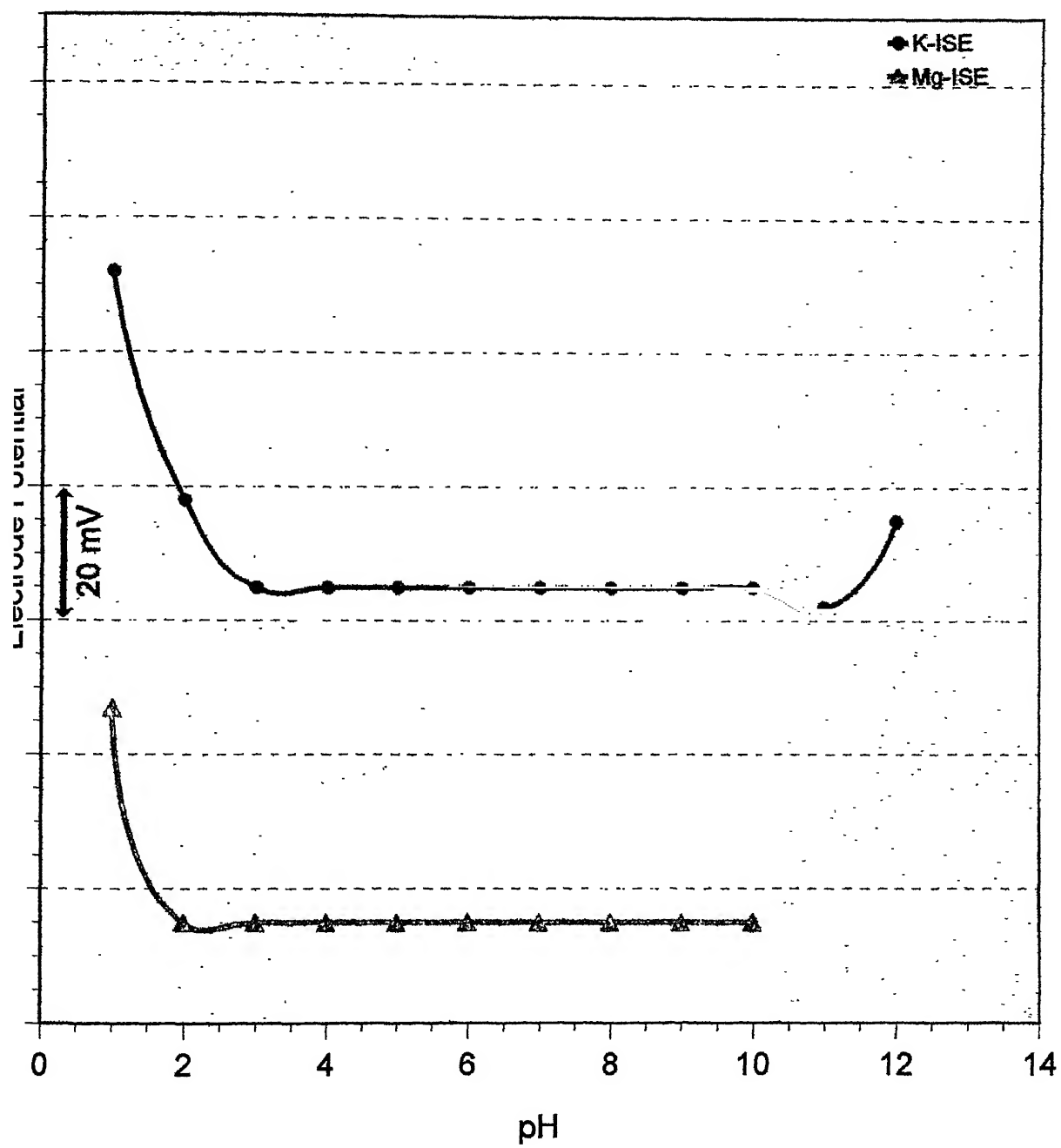


FIG. 4.3 : Potential vs. pH



4.2.2.5 Life Time

It was observed the electrode gave stable potential up to 5 months. After this time the electrode gives erratic response. Therefore, the life time of K(I) ISE is 5 months.

4.2.3 Applications

To see the utility of the electrode prepared, the electrode was used as an indicator electrode in the precipitation titration and also used in the direct determination of soil samples.

4.2.3.1 Titration of Potassium Nitrate against Sodium Tetraphenyl Borate

For this 5 ml of 0.01 mol dm⁻³ KNO₃ solution was taken in a beaker and volume was raised 20 ml with distilled water. The beaker was kept on a magnetic stirrer and the electrode assembly was dipped in beaker. This solution was titrated against 0.01 mol dm⁻³ of sodium tetraphenyl borate and the potential was recorded after each addition of a small volume of titrant (Table 4.5). The electrode potential was plotted against the volume of titrant consumed. (Fig. 4.4). It can be seen from the titration curve that there is a sudden jump of potential near the end point of titration, which makes the electrode, a good indicator electrode for the precipitation titration.

4.2.3.2 Determination of Potassium in Soils

Mortland (19) extracted the exchangeable potassium from soils with a 0.05M magnesium acetate solution, and determined it with K(I) sensitive glass electrode. T.R.Yu (20) and subsequently Zhang and Wang (21) and Yi (22) extracted the exchangeable potassium with a 0.5M barium chloride, and determined it with a PVC-type liquid state membrane electrode using a crown compound a electroactive material.

Table : 4.5**Titration of Potassium Nitrate against Sodium Tetraphenyl
Borate**

Volume of Titrant (ml)	Electrode Potential (mV)
0.0	35
0.5	35
1.0	35
1.5	36
2.0	36
2.5	37
3.0	40
3.5	44
4.0	48
4.5	55
5.0	120
5.5	125
6.0	130
6.5	131
7.0	133
7.5	135
8.0	136
8.5	136
9.0	136
10.0	136

In this work soil samples were collected from the different parts of India as described in chapter 2. The six soil samples were taken for determination of potassium ion. 1.0 g of each soil sample S₁, S₂, S₃, S₄, S₅ or S₆ was used for the preparation of soil extract as described in chapter 2. The pH of all the solutions were checked and it

FIG. 4.4 : Titration of Potassium Nitrate
vs Sodium Tetraphenyl Borate

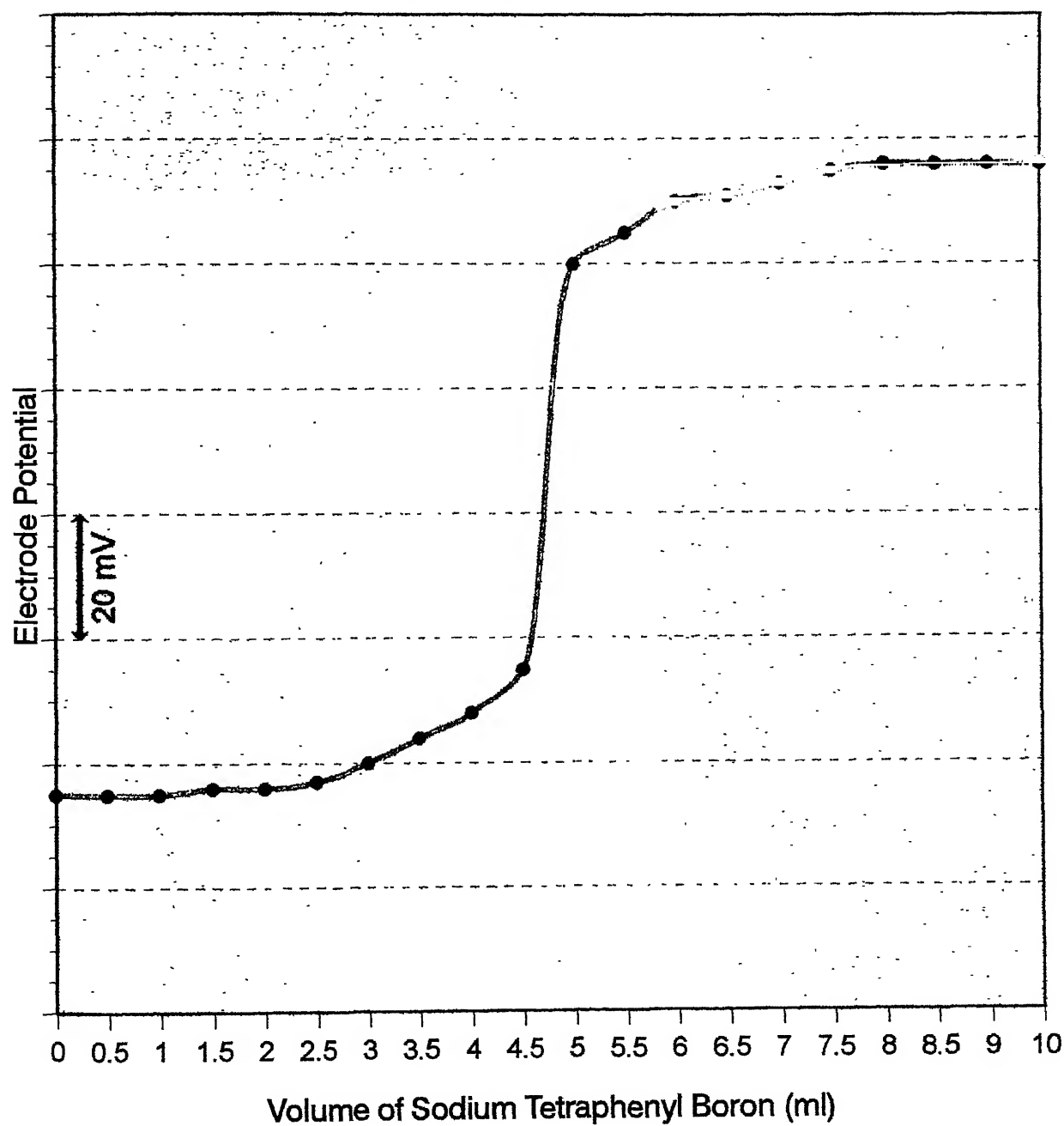


FIG. 4.5 : Determination of K(I) Ion in Soil Samples

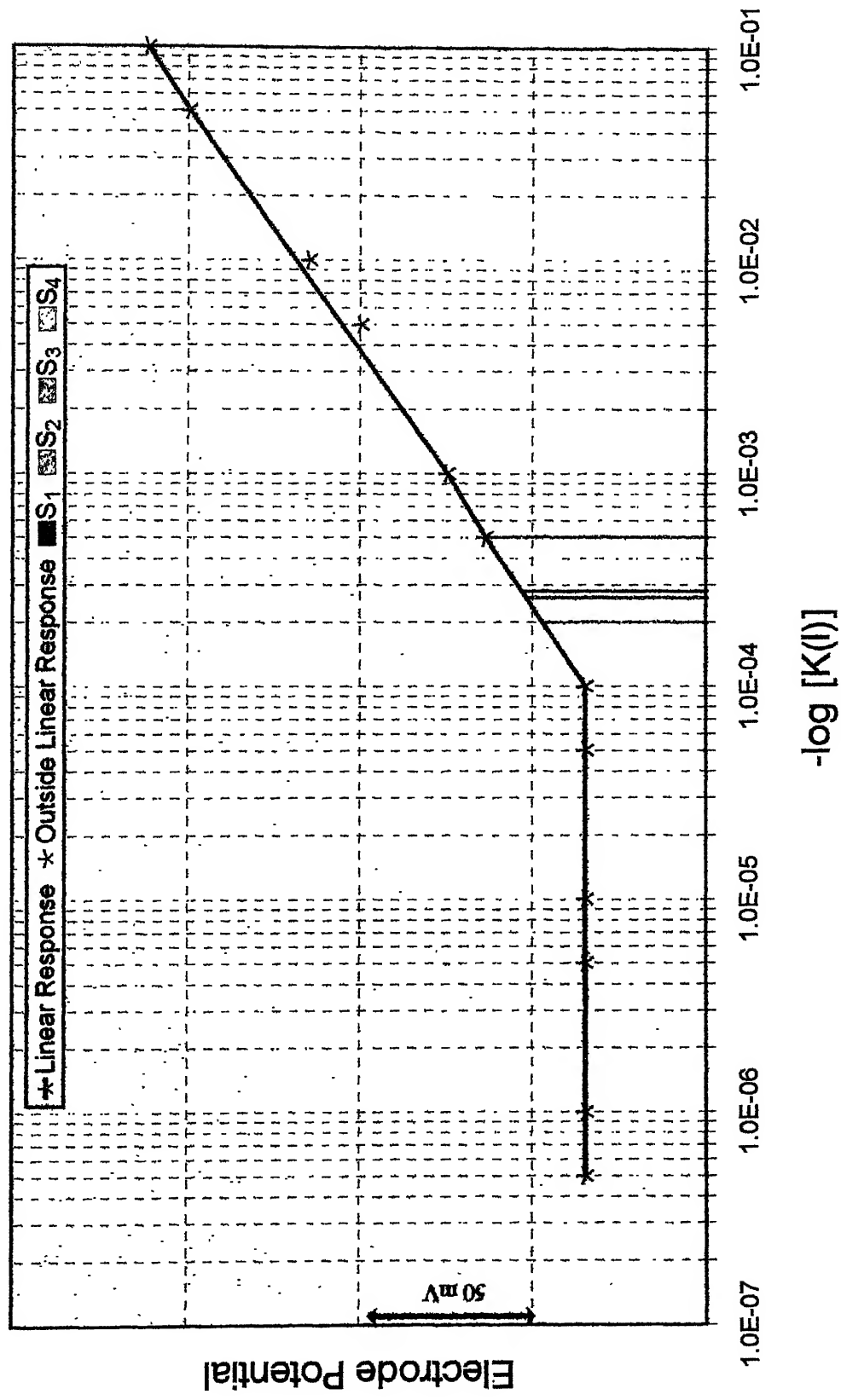
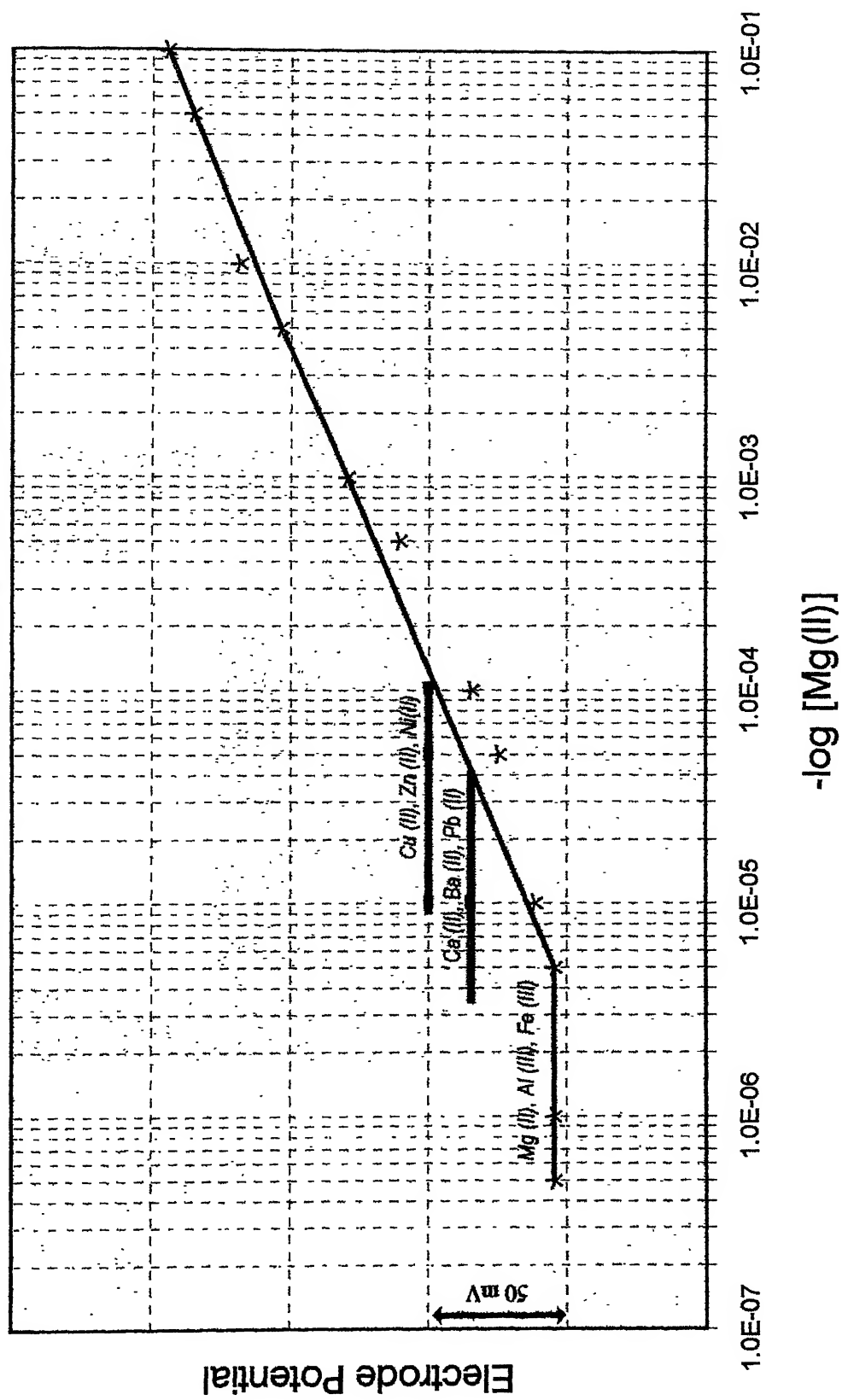


FIG. 4.6 : Potential vs $-\log$ Concentration of Mg(II) Ion
in Presence and Absence of Secondary Ions



was found that the pH was within the working range of the electrode. Each solution was made up to 100 ml by adding distilled water. Now the potential of each soil solution was recorded (Table 4.6) and the amount of potassium present in the soil sample was determined from the calibration curve (Table 4.6 and Fig. 4.5).

The same soil solutions were also used for atomic absorption analysis. For this, the analysis was carried out at the Research and Development Laboratory, IFFCO, Phulpur. For determination of potassium content in soils the wavelength (λ_{max}) was set at 766.5 nm and slit was 0.7 nm while the air acetylene flame was used.

Table : 4.6
Analysis of Soils

Sample	Electrode Potential (mV)	Amount of K(I) by ISE (ppm)	Amount K(I) by AAS (ppm)
S ₁	153	10.92	10.60
S ₂	152	10.14	10.20
S ₃	164	19.50	19.00
S ₄	147	7.80	8.80
S ₅	—	—	2.20
S ₆	—	—	2.60

The amount of potassium was calculated by the calibrations curve. The potassium contents of soil samples S₁ to S₄ was higher than the potassium content of samples S₅ and S₆ as revealed by AAS values (Table 4.6). For sample S₅ and S₆ the potential of ISE does not fall on the linear range curve, owing to the low potassium content of the samples and therefore, the values could not be determined by ISE method. However the potassium content of samples S₁ to S₄ determined by both the methods agree well with each other.

4.3 MAGNESIUM ION SELECTIVE ELECTRODE

A brief survey of literature, preparation of a new Mg(II) ISE, its characteristics and applications are the main highlights of this

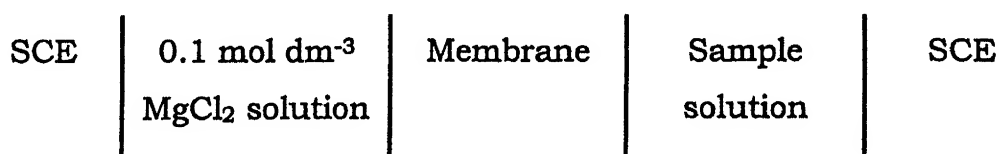
section. Sharp (23) prepared a electrode with a parquet-type polymer of tetracyano-ethylene (TCNE) containing magnesium. The electrode was little selective over calcium, sodium and potassium ions while zinc, nickel and copper ions interfered. The bivalent cation electrode has been employed for the determination of magnesium ion in fresh and sea (24-29) waters and in soils for the determination of water hardness. Magnesium oxinate ISE was prepared by Mishra and Chattopadhyaya (30) using epoxy resin.

4.3.1 Preparation of Electrode

The details of preparation of electroactive material the *magnesium complex of p-dimethyl amino-azobenzene sulfonate* has been described in chapter 3. This electroactive material mixed with epoxy resin in 1:4 ratio and a master membrane was formed as described in chapter 2. From the membrane a small piece was cut and plugged into the end of the barrel shaped tube which was filled with $0.1 \text{ mol dm}^{-3} \text{ MgCl}_2$ as reference solution. A saturated calomel electrode was inserted inside the tube for electrical contact and a secondary calomel electrode was also used along with electrode as a reference electrode.

4.3.2 Characteristics of Electrode

The electrode thus fabricated was dipped in 0.01 mol dm^{-3} solution of MgCl_2 for 10 days, so that it attained the stability. After conditioning the electrode various parameters were determined at room temperature ($25 \pm 2^\circ$). A Philips pH meter (PR 9405) was used for measurements. The electrode assembly can be represented as :



The following characteristics were studied.

4.3.2.1 Electrode Response

For determination of electrode response a series of solutions of varying concentrations from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ of

Mg(II) ions were prepared. The electrode potential of each solution was recorded (Table 4.1) with the help of ISE prepared and then the concentrations of ions were plotted against the electrode potentials on a semilog graph paper (Fig. 4.6).

From the graph it was clear that the linear response was obtained down to magnesium (II) ion concentration $5 \times 10^{-6} \text{ mol dm}^{-3}$ with a slope 33 mV per-decade change in Mg (II) ion concentration.

4.3.2.2 Response Time

The concentration of Mg (II) ion was varied from 0.1 mol dm^{-3} to 0.01 mol dm^{-3} and the change in potentials were noted (Table 4.2) at the interval of 5 seconds. These potentials were plotted against time (Fig. 4.2) and it was found that after 20 seconds the ISE attained a constant potential. Thus the response time for the electrode is 20 seconds.

4.3.2.3 Effect of pH

A set of solutions were prepared in which the Mg (II) ion concentration was kept constant at 0.01 mol dm^{-3} and the pH was varied from 1 to 12. The potential of each solution was recorded (Table 4.3) and then plotted against the pH (Fig. 4.3). It was observed from the graph that pH 2 to 9 the electrode potential remains constant. Thus, the working pH range of electrode is 2 to 9.

4.3.2.4 Selectivity Coefficient

For determination of selectivity coefficient by mixed solution method, a series of solutions of Mg (II) ion were prepared in which the concentration of interfering ion was kept constant ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and the concentration of Mg (II) ions varied from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$. The potential of each solution was noted (Table 4.4) and plotted against the concentration of Mg (II) ion on a semi-log graph paper (Fig. 4.6). The selectivity coefficients were calculated from graph and are given in (Table 4.4).

4.3.2.5 Life Time

It was observed that the electrode give stable potential even after the use of electrode was 4 months. After which it starts behaviour with erratically. Thus 4 months time could be termed as life time of the electrode.

4.3.3 Applications

To see the utility of electrode prepared, the electrode was used as an indicator electrode in the precipitation titration. The electrode was also used for the direct determination of Mg (II) ion in naturally occurring minerals and soil samples. For direct determination of magnesium content in the samples by above prepared ISE the following minerals were taken *dolomite, magnesite and soils*.

4.3.3.1 Titration of Magnesium Chloride against Disodium Hydrogen Phosphate

The Mg (II) ISE was used as an indicator electrode in the precipitation titration of 0.01 mol dm^{-3} MgCl_2 against 0.01 mol dm^{-3} Na_2HPO_4 . For this 10 ml of 0.01 mol dm^{-3} MgCl_2 solution was taken in a beaker along with magnetic bar the beaker was placed on magnetic stirrer. The titrant was gradually added into the beaker from the micro burette and electrode potential was measured (Table 4.7) after each addition of small volume of titrant. These potentials were plotted against the volume of titrant consumed (Fig. 4.7).

It may be seen in the titration curve that there is a sharp rise of potential at the equivalence point. Thus the electrode could be used as indicator electrode in the precipitation titration.

4.3.3.2 Determination of Magnesium In Dolomite

Three different types of dolomites were studied (chapter 2). For determination of Mg (II) ion in dolomites, 0.5g and 1.0g samples of dolomite A, dolomite B and 1.0g and 2.0g of dolomite C were taken in separate beakers. Each of these sample was treated with 2 ml of 1:1 sulphuric and 5ml of concentrated hydrofluoric acids. The solutions were heated to copious fumes and cooled. After cooling the sample, 10

ml of distilled water was added to wash down the samples adhering to the walls of the beaker. The solution was again evaporated to copious fumes. The solutions were cooled and pH was adjusted to the working range of electrode by adding few drops of dil NaOH. Then the solutions were made up to 100 ml by distilled water, and the potential of each solution was recorded (Table 4.8). The amount of Mg (II) ion was calculated from the calibration curve (Fig. 4.8 and 4.9). These values were then compared with the values obtained from the XRF by the courtesy of Saurashtra Cement Factory, Gujrat (Table 4.8).

It was observed that there is a good agreement between the values obtained from both the methods.

Table: 4.7
Titration of Magnesium Chloride against Disodium Hydrogen Phosphate

Volume of titrant (ml)	Electrode Potential (mV)
0.0	35
1.0	36
2.0	37
3.0	38
4.0	40
5.0	44
6.0	50
7.0	53
7.5	56
8.0	60
8.5	63
9.0	70
9.5	75
10.0	136
10.5	145
11.0	150
11.5	154
12.0	160
13.0	163
14.0	165
15.0	165

**FIG. 4.7 : Titration of Magnesium Chloride vs
Disodium Hydrogen Phosphate**

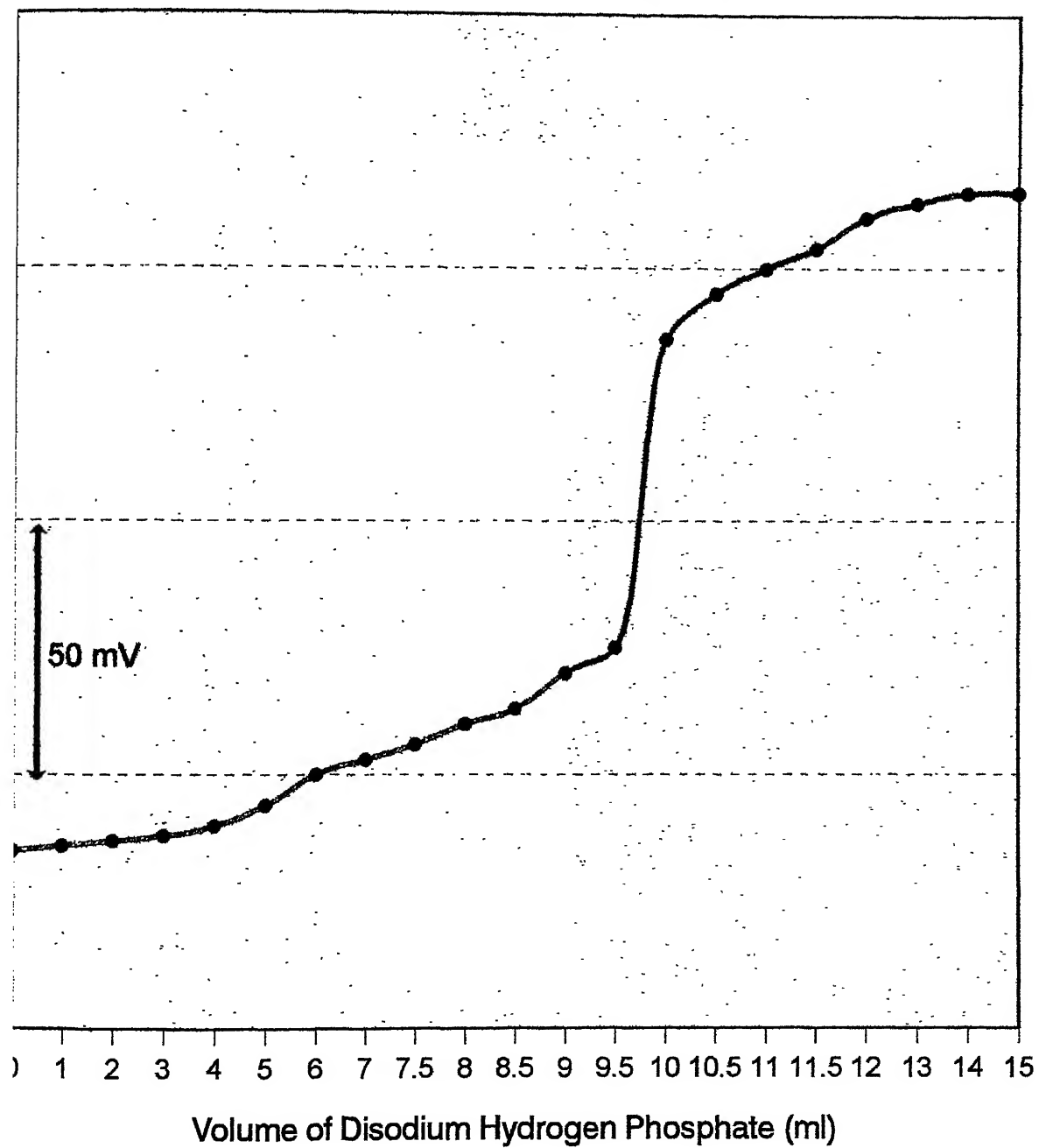


FIG. 4.8 : Determination of Mg(II) Ion in Dolomite A and Dolomite B

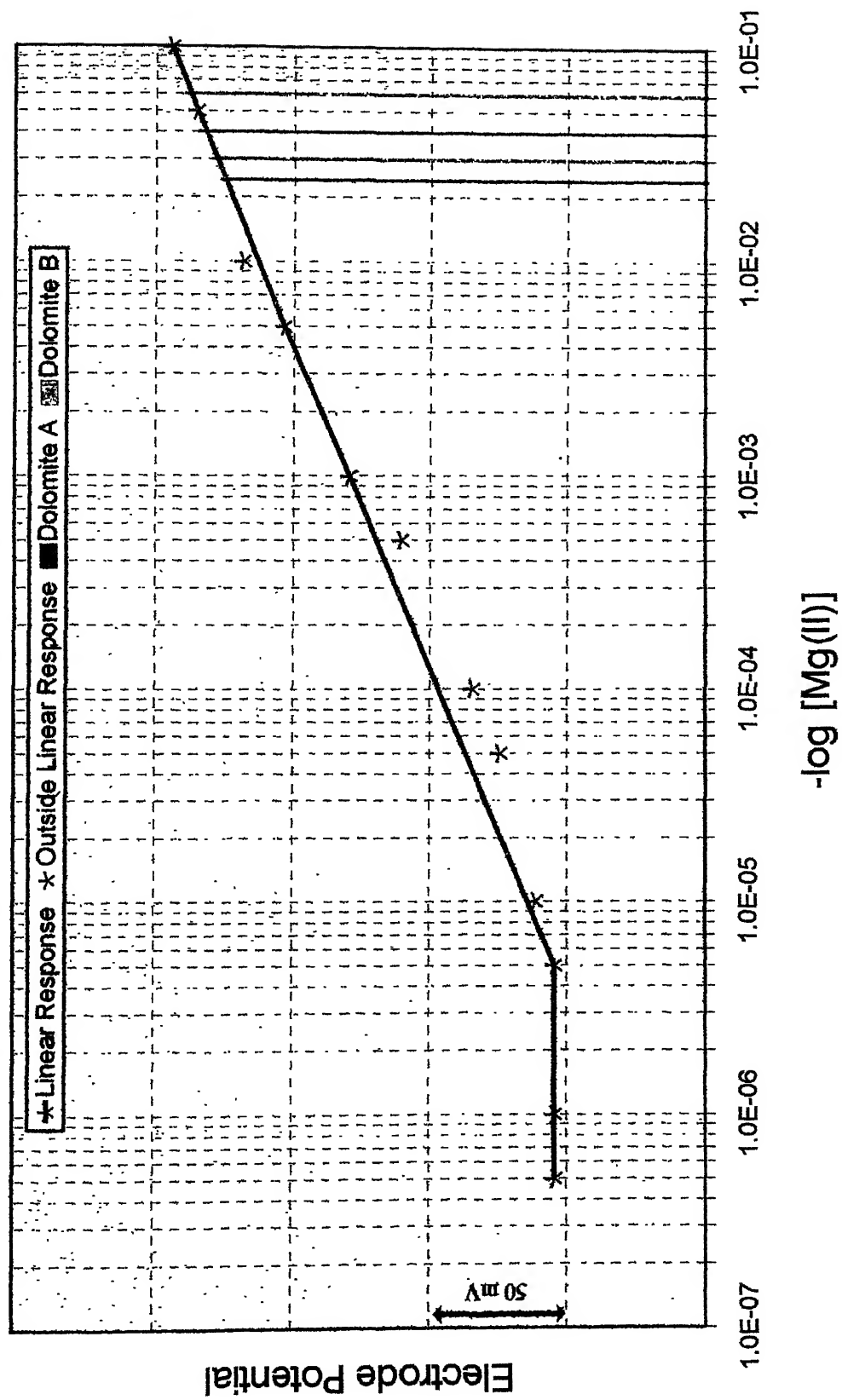


FIG. 4.9 : Determination of Mg(II) Ion in Dolomite C and Magnesite

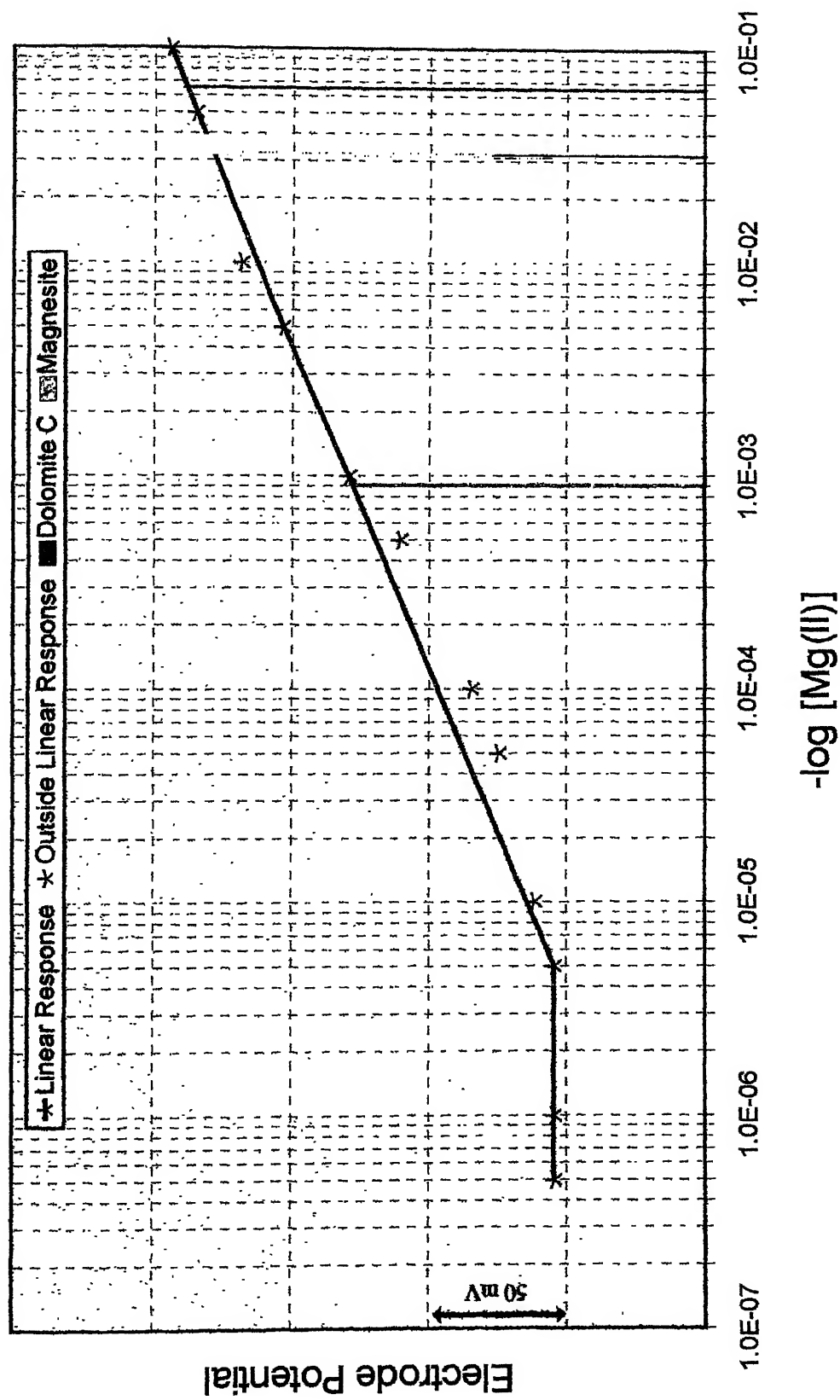


Table: 4.8
Analysis of Dolomite

Sample	Weighed Amount of Sample (g)	Electrode Potential (mV)	Amount of Mg(II) by ISE (g)	Amount of Mg(II) by XRF (g)
Dolomite A	0.5	177	0.0608	0.0612
	1.0	185	0.1216	0.1224
Dolomite B	0.5	180	0.0729	0.0759
	1.0	190	0.1459	0.1518
Dolomite C	1.0	180	0.0780	0.0780
	2.0	199	0.1580	0.1560

4.3.3.3 Determination of Magnesium in Magnesite

The Mg (II) ion content in magnesite was determined by Mokra and Henek (34) by potentiometric titration technique using Cu (II) ISE as an indicator electrode. In the present work the Mg (II) ISE has been used as an indicator electrode for the direct determination of Mg (II) content in magnesite.

0.5g magnesite was taken in beaker and treated with 5 ml of concentrated hydrochloric acid. The beaker was heated to evaporate the solution to dryness. After cooling the beaker the residue was digested with 10 ml of distilled water followed by few drops of hydrochloric acid. The mixture was heated to boiling and then it was cooled and filtered. The pH of the filtrate was checked and was found within the working range of electrode. Then the solution was made up to 100 ml and the potential was recorded 128mV. This value was converted into concentration of Mg (II) ion and, the amount of Mg(II) found in the 0.5g of the sample was 21.879 ppm from the calibration curve (Fig. 4.9).

In order to find out the validity of the method the amount of mg(II) in the magnesite sample was also determined by AAS technique

at Research and Development Laboratory, IFFCO, Phulpur. For determination the wavelength (λ_{\max}) was set at 285.2 nm and slit 0.7 nm. The air acetylene flame was used. The value of magnesium content determined by this way, 21.6 ppm, agreed fairly well with the value determined by ISE method noted above.

Thus the electrode could be used for the direct determination of magnesium in magnesite.

4.3.3.4 Determination of Magnesium in Soils

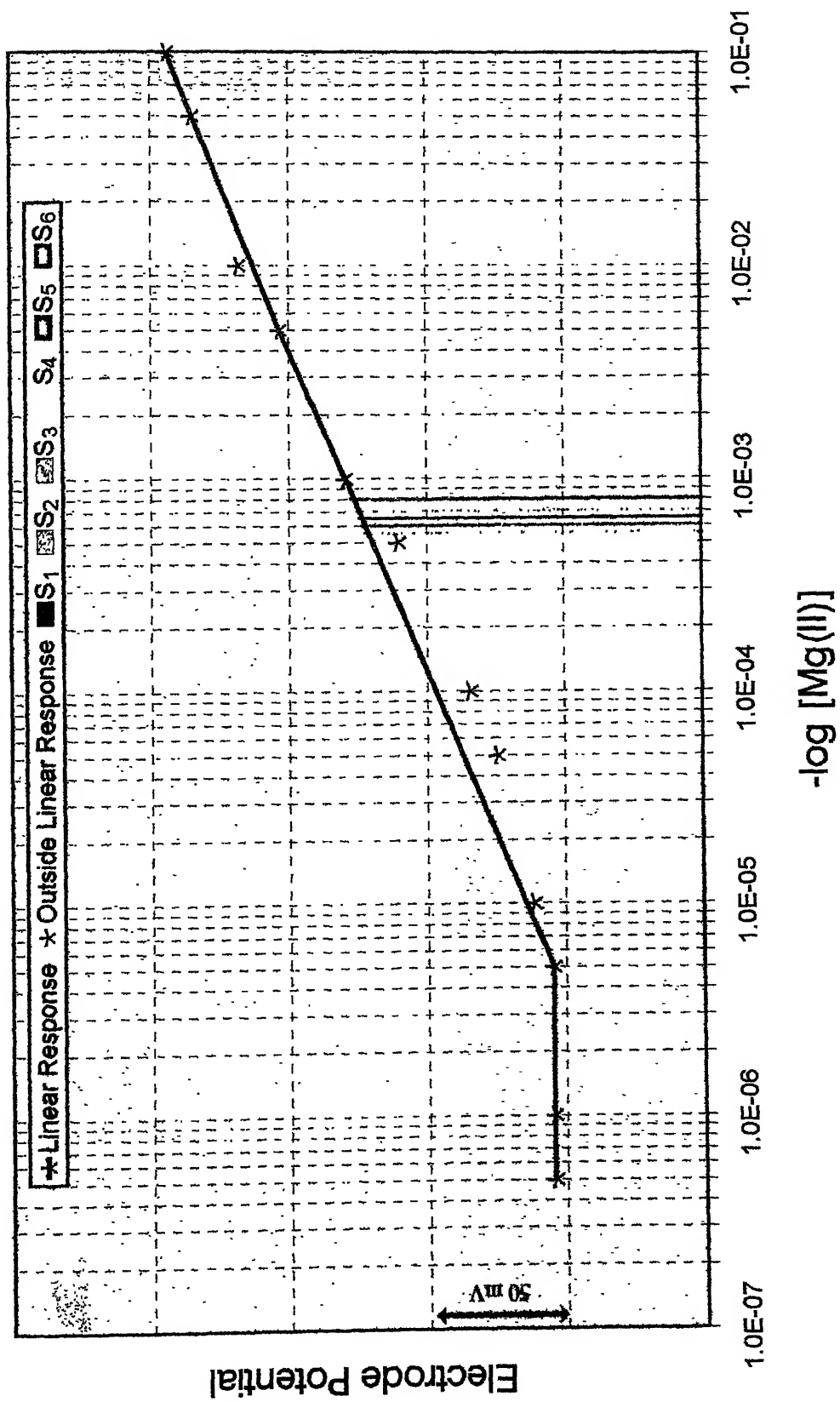
The six soil samples described in chapter 2 were studied for the determination of Mg (II) ion in soil samples. 1.0 g of all the six soils, S₁, S₂, S₃, S₄, S₅ and S₆ were taken in different beakers. The soil extract was prepared using the method described earlier in chapter 2. Then the pH of all the soil solutions were noted and it was found that the pH was within the working range of electrode. The potential of each solution was recorded (Table 4.9) and the amount of Mg(II) was calculated from the calibration curve (Fig. 4.10).

The amount of Mg (II) ion was also determined by AAS technique at Research and Development Laboratory, IFFCO, Phulpur. For this the wavelength (λ_{\max}) was set at 285.2 nm and slit 0.7 nm while air acetylene flame was used.

Table: 4.9
Analysis of Soils

Soil Samples	Electrode Potential (mV)	Amount of Mg (II) by ISE (ppm)	Amount of Mg (II) by AAS (ppm)
S ₁	125	15.80	16.30
S ₂	124	14.59	15.80
S ₃	128	17.00	17.40
S ₄	121	12.16	12.60
S ₅	123	13.37	13.30
S ₆	124	14.01	13.80

FIG. 4.10 : Determination of Mg(II) Ion in Soils

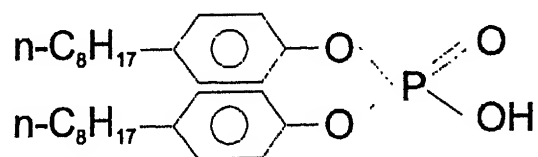


The values obtained from ISE method and AAS studied are compared in Table 4.9. From which it is clear that there is a good agreement between the amounts of magnesium determined by both the techniques. Thus the electrode method could be applied for the direct determination of magnesium in soil samples.

4.4 CALCIUM ION SELECTIVE ELECTRODE

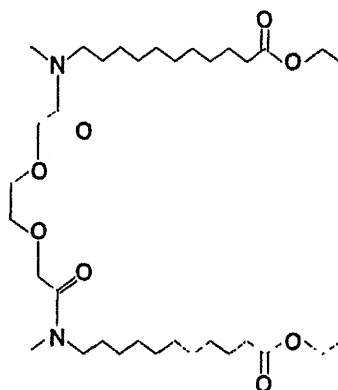
Calcium selective electrodes are a good example of development of ISEs towards greater selectivity. The first analytically useful Ca (II) ISE, was described by Ross (35). Another step ahead was the preparation of PVC membranes with esters of alkyl phosphoric acids by Thomas *et al.* (37,37). A mixture of 28.8% w/w PVC + 71.2 w/w of dicotyl phenyl phosphonate and mono-calcium dihydrogen tetra (didecylphosphate) in a ratio of 10:1 was found to be the best for preparation of PVC membranes (36). PVC membranes were also used earlier in Ca²⁺ LISE's containing 2-thenoyltrifluoroacetone and tributyl phosphate as a plasticizer (38-40), other versions of electrodes with this ion-exchanger are also possible (41). According to Shatkay, these electrodes are comparable with the Orion 92-20 electrode (39) and retain the Ca²⁺ response up to 100-200 fold ration of Na⁺ and NH₄⁺ to Ca²⁺ (40).

First Růžicka *et al.* (42,43) have used calcium bis (di-n-octyl phenyl phosphate) salat (DOPP exchanger) in dioctyl phenyl phosphonate solvent. The new electrode exhibited substantially lower selectivity coefficients for H₃O⁺ and other univalent ions and a lower detection limit.



di-n-octylphenylphosphoric acid

Simon and co-workers (44-47) described improved electrodes based on acyclic, lipophilic legends (neutral ion carriers), with a structure, which can be schematically depicted as:



The performance of earlier neutral carrier electrodes (44) did not give satisfactory performance as the detection limit was 10^{-4} mol dm⁻³ in dilute calcium solutions. There are several variations of Ca (II) ISEs containing esters of phosphoric acid have been described (48-57). Calcium gives precipitate with sodium rhodizonate and this precipitate has been used for developing a sensor for rhodizonate ion (58). Rhodizonates of Ba and Ca have also been used as electroactive materials for preparation of Sr and Ba sensors (59,60). The calcium rhodizonate has been also used as electroactive material for fabrication of Ca (II) ISE (60).

In this work two more precipitates of Ca (II) ion namely *calcium succinate* and *calcium citrate* have been used as an electroactive material for developing new Ca (II) ISEs.

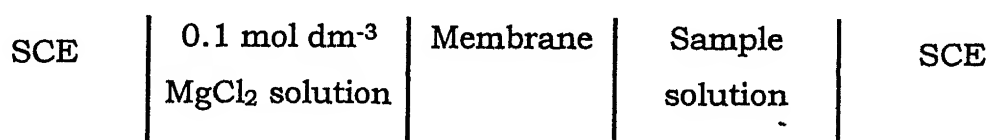
4.4.1 Preparation of Electrodes

The electroactive materials *Calcium succinate* and *Calcium citrate* were prepared as described in chapter 3. Each of these electroactive materials were converted into a master membrane 0.5 mm thickness using epoxy resin as binder by method described in chapter 2. From master membranes the Ca (II) ISEs were fabricated by plugging a portion of the membrane at one end of the barrel shaped tube. The tube was filled with internal reference solution of 0.1 mol

dm^{-3} CaCl_2 and inserted a saturated calomel electrode inside both the tubes. The electrode containing *calcium succinate* as electroactive material is designated as *electrode I* and *calcium citrate* as electroactive material as *electrode II*.

Both *electrodes I* and *II* were kept immersed in solution of 0.01 mol dm^{-3} of CaCl_2 solution for 10 days for conditioned the electrode. After conditioning, the electrode gave constant potential.

Both the electrode systems could be represented as



4.4.2 Characteristics of Electrodes

A Philips pH meter (PR 9405) was used for all the measurements. The measurements were carried out at room temperature ($25 \pm 2^\circ$). The following characteristics of electrodes were studied.

4.4.2.1 Electrode Response

To determine the electrode response of Ca(II) ISEs, a series of solutions of varying concentrations from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ for Ca (II) ion were prepared. The electrode potentials of all the solutions were recorded using both the electrodes (Table 4.10) and the concentration of Ca (II) were plotted against potentials in both cases. From the graph it is clear that the linear response of *electrode-I* was down to $1 \times 10^{-4} \text{ mol dm}^{-3}$ with slope 44 mV per-decade change in Ca (II) ion concentration (Fig. 4.11). Incase of *electrode-II* the linear response was down to $5 \times 10^{-5} \text{ mol dm}^{-3}$ with slope 35 mV per-decade change in Ca (II) ion concentration (Fig. 4.12).

4.4.2.2 Response Time

The concentration of Ca (II) ion was varied from 0.1 mol dm^{-3} to 0.01 mol dm^{-3} and change in potential was noted (Table 4.11) for both the electrodes at the interval of 5 second. These potentials were

plotted against time (Fig. 4.13) and it was found that a constant potential was allowed after 25 seconds for *electrode I* and 20 seconds for *electrode II*. which could be denoted as the response time for respective electrodes.

4.4.2.3 Effect of pH

The Ca (II) ion concentration was kept constant 0.01 mol dm^{-3} and the pH was varied form 1 to 12. The potential of each solution was recorded (Table 4.12) for both the electrodes and potted against pH (Fig. 4.14). It is observed from the graph that the working range for both the electrodes is 2 to 10.

Table: 4.10
Electrode Response

Concentration of Ca(II) ion (mol dm^{-3})	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
1×10^{-1}	288	215
5×10^{-2}	275	203
1×10^{-2}	240	180
5×10^{-3}	230	160
1×10^{-3}	195	137
5×10^{-4}	180	125
1×10^{-4}	150	95
5×10^{-5}	150	87
1×10^{-5}	150	87
5×10^{-6}	150	87
1×10^{-6}	150	87

4.4.2.4 Selectively Coefficient

For determination of selectively coefficient a series of solution was prepared in which the concentration of interfering ion was kept constant ($1 \times 10^{-3} \text{ mol dm}^{-3}$) while concentration of Ca (II) ion was varied. The potential of each solution was noted and plotted against

concentration on a semilog graph paper (Fig. 4.11 and 4.12). The selectivity coefficient was then calculated as usual and values are given in Table 4.13.

Table: 4.11
Response Time

Time (sec)	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0	288	217
5	270	200
10	260	195
15	250	185
20	245	180
25	240	180
30	240	180
35	240	180
40	240	180

Table: 4.12
Effect of pH

pH	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
1	85	65
2	105	88
3	111	90
4	111	90
5	111	90
6	111	90
7	110	90
8	111	88
9	111	90
10	111	90

FIG. 4.11 : Potential vs -log Concentration of Ca(II) Ion
in Presence and Absence of Secondary Ions

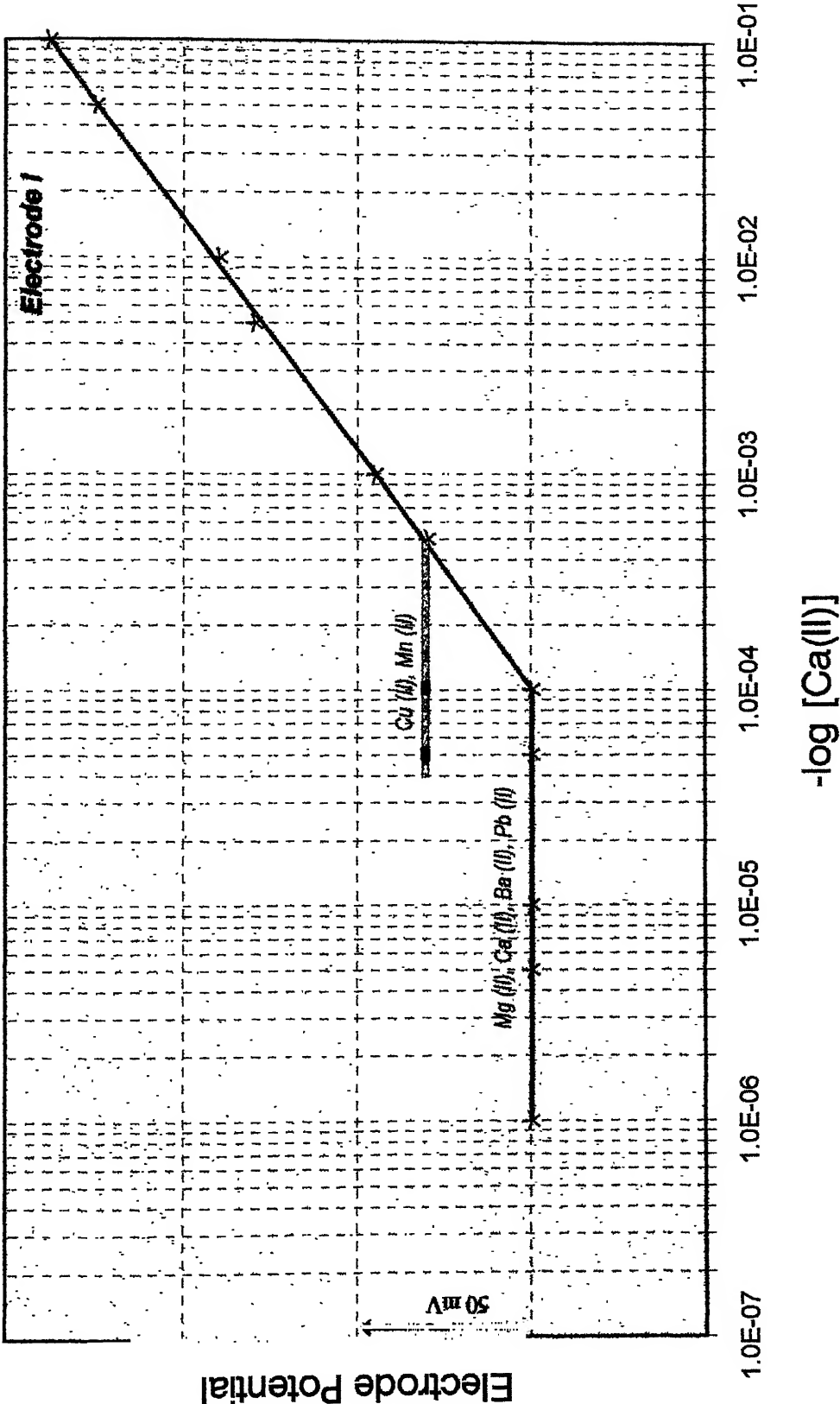


FIG. 4.12 : Potential vs $-\log$ Concentration of Ca(II) Ion
in Presence and Absence of Secondary Ions

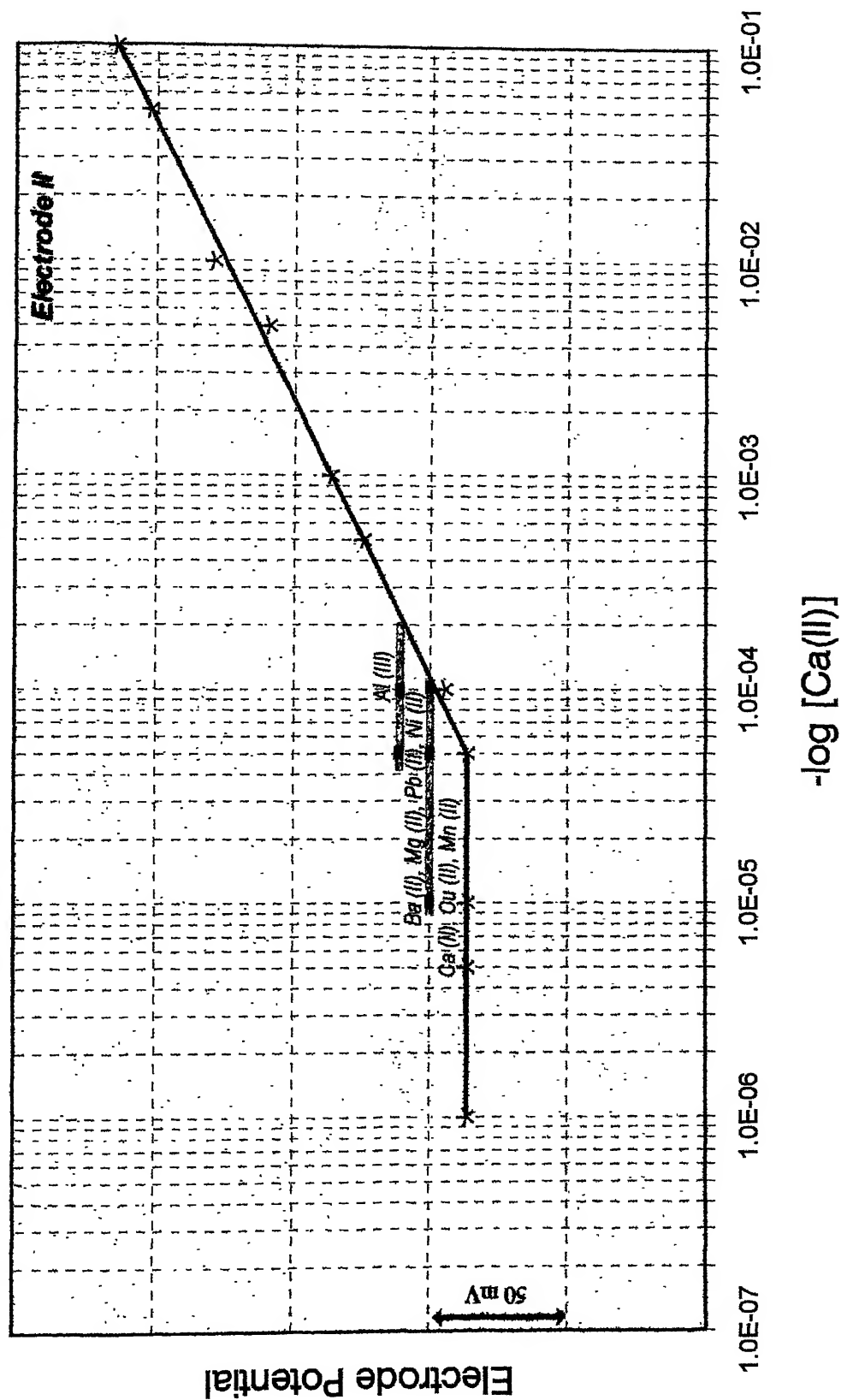


FIG. 4.13 : Potential vs Time

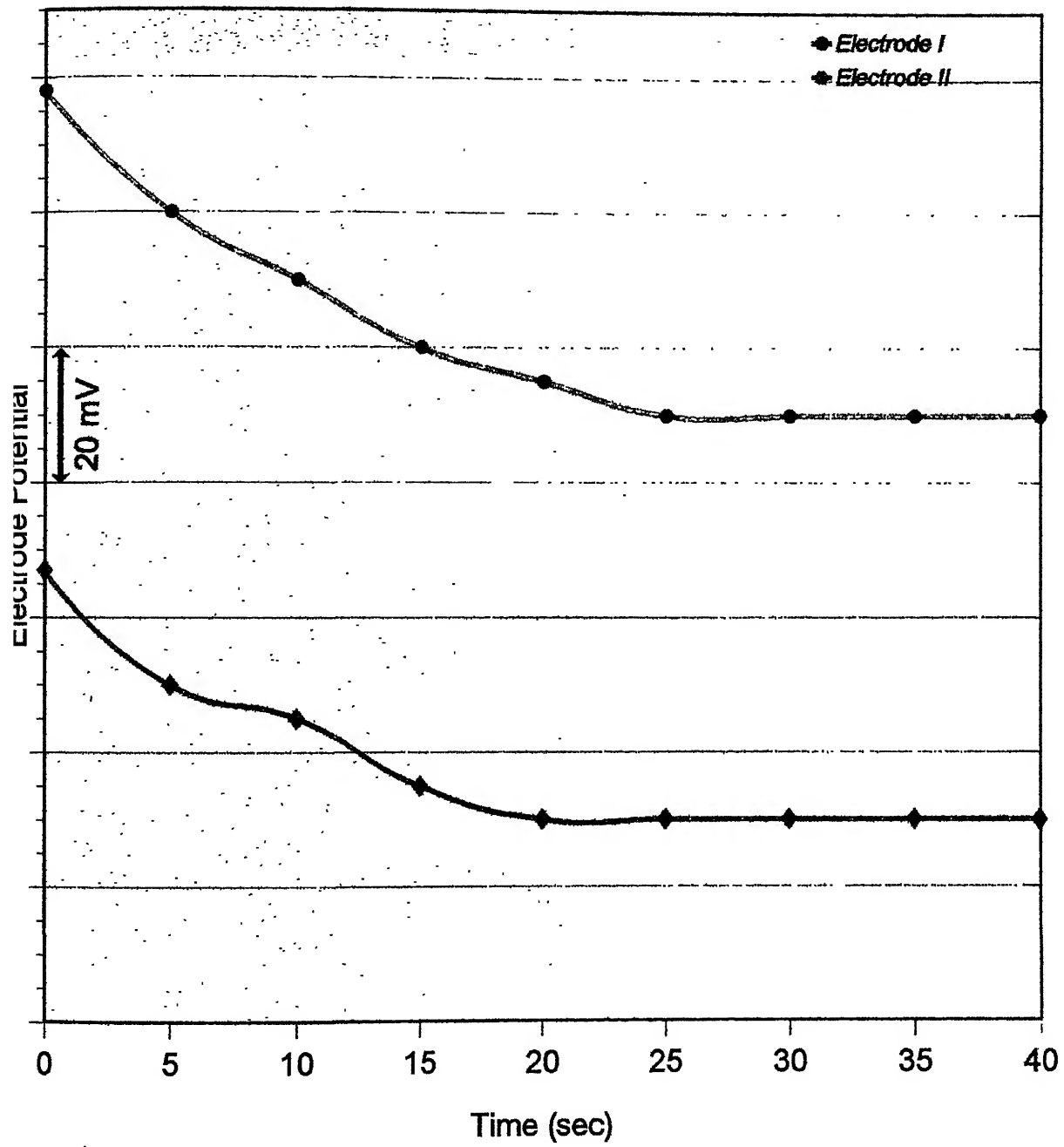


FIG. 4.14 : Potential vs pH

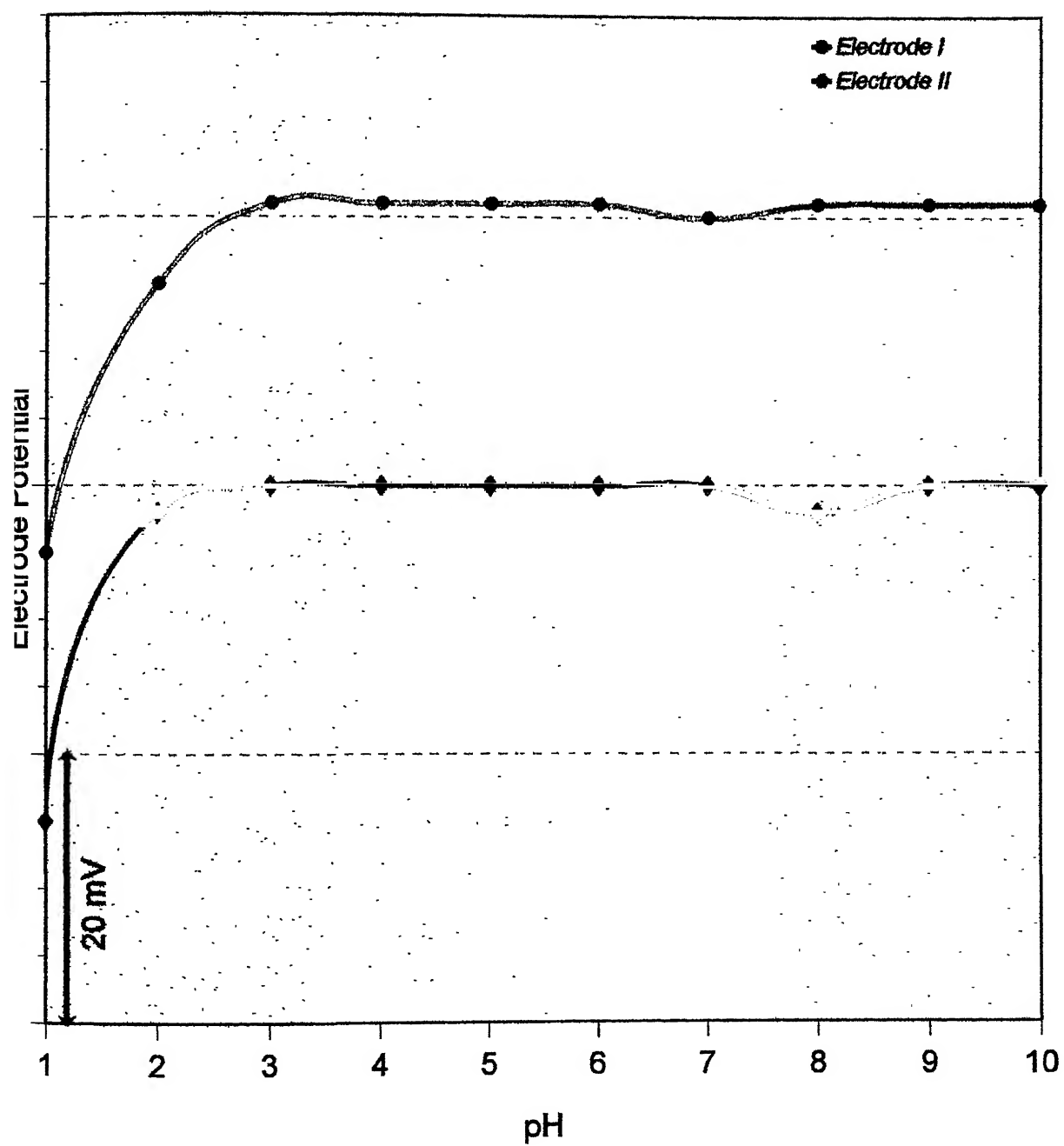


Table: 4.13
Selectively Coefficient

Ions	$K_{Ca^{2+},M}^{pot}$ <i>Electrode I</i>	$K_{Ca^{2+},M}^{pot}$ <i>Electrode II</i>
Al (III)	0.02	—
Ba (II)	0.10	0.1
Mg (II)	0.10	0.1
Pb (II)	0.10	0.1
Ni (II)	0.10	0.1
Cu (II)	0.50	0.5
Mn (II)	0.50	0.5

4.4.2.5 Life Time

The electrode response remain constant up to a period of 5 months in both cases but after this period both the electrodes started giving erratic results. Thus 5 months time could be safely termed as the lifetime of each electrode.

4.4.3 Applications

To see the utility of electrodes prepared, the electrodes were used as an indicator electrode in the precipitation titration. The electrodes were also used for the direct determination of Ca (II) ion in naturally occurring minerals *limestone, calcite, chalk* and *soils*.

4.4.3.1 Titration of Calcium Chloride against Sodium Palmitate

5ml of 0.01 mol dm⁻³ CaCl₂ solution was taken in a beaker and titrated against 0.01 mol dm⁻³ sodium palmitate (C₁₅H₃₁COONa) solution. The potentials were noted by using both the electrodes after each addition of small volume of titrant (Table 4.14). These values were plotted against the titrant consumed (Fig. 4.15).

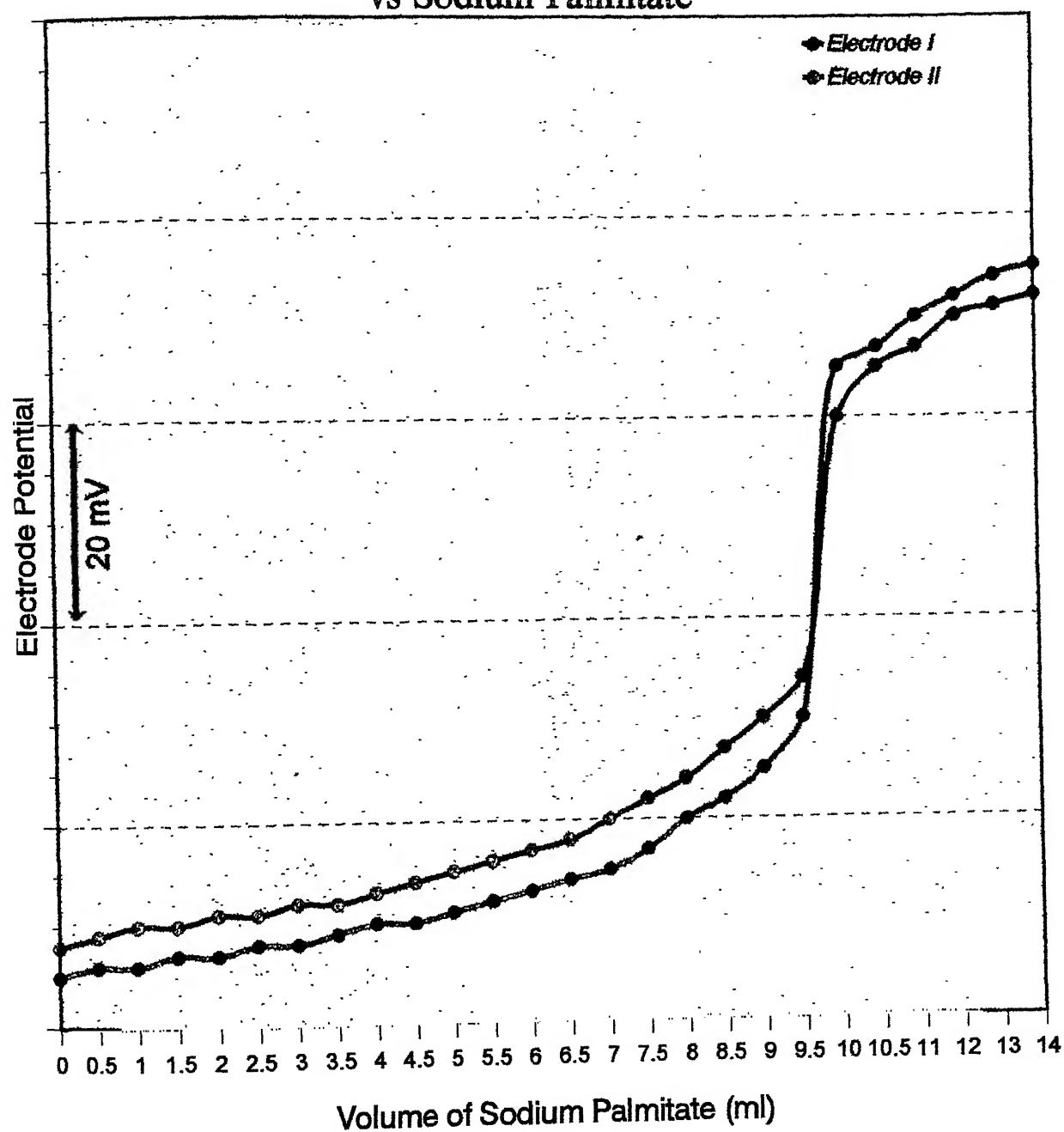
It can be seen from the titration curve that there is a sudden jump of potential near the end point, which establishes that both the

electrodes can serve as good indicator electrode for precipitation titration.

Table: 4.14
Titration of Calcium Chloride against Sodium Palmitate

Volume of Titrant (ml)	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0.0	55	58
0.5	56	59
1.0	56	60
1.5	57	60
2.0	57	61
2.5	58	61
3.0	58	62
3.5	59	62
4.0	60	63
4.5	60	64
5.0	61	65
5.5	62	66
6.0	63	67
6.5	64	68
7.0	65	70
7.5	67	72
8.0	70	74
8.5	72	77
9.0	75	80
9.5	80	84
10.0	115	110
10.5	117	115
11.0	120	117
12.0	122	120
13.0	124	121
14.0	125	122

FIG. 4.15 : Titration of Calcium Chloride
vs Sodium Palmitate



4.4.3.2 Determination of Calcium in Limestone

Limestone consists mainly of calcium carbonate. It is the raw material used in the manufacture of lime and its analysis is widely performed in routine control work. In addition to calcium carbonate, limestone usually contains varying amount of magnesium and smaller proportions of silica, iron, aluminium and manganese and often phosphorus, sulphur, titanium and the alkalis. The content of calcium in limestone was determined by Chalk and Keeney (61) using the ISE method.

For this 0.2g and 0.5g limestone samples described in chapter 2, was taken in different beakers and treated with 2ml of 1:1 sulphuric acid and 5 ml of concentrated hydrofluoric acid. The solution was heated to copious fumes and cooled, washed down the sides with 10 ml of distilled water and again evaporated to copious fumes. After cooling, the pH of the each solution was checked and adjusted to working pH range of the electrode by adding dil NaOH. The solution was made up to 100ml by adding distilled water. Then the potential of each solution was recorded using prepared *electrode II* and the content of calcium present in limestone was calculated from the calibration curve (Table 4.15 and Fig. 4.16).

Table: 4.15
Analysis of Limestone

Weighted Amount of Limestone (g)	Electrode Potential (mV)	Amount of Ca (II) by ISE (g)	Amount of Ca (II) by XRF (g)
0.2	186	0.0720	0.0749
0.5	202	0.1800	0.1874

In order to establish the validity of the method the calcium content in limestone sample was also determined by XRF method by the courtesy of Saurashtra Cement Factory, Gujrat and are compared in Table 4.15. The agreement of values establishes that the direct determination of Ca (II) ion by ISE a useful and reliable method.

4.4.3.3 Determination of Calcium in Calcite and Chalk

Calcite and chalk are the most common naturally occurring mineral of calcium. In present work naturally occurring calcite (described in chapter 2) and common chalk were studied.

0.5g calcite was treated with 1:1 sulphuric and 5 ml of concentrated hydrofluoric acids. The solution was heated to copious fumes and cooled. After cooling 10 ml of distilled water was added into beaker and again evaporated to copious fumes. Then beaker was cooled and pH was adjusted to the working pH range of electrode by adding dil NaOH and solution was made up to 100ml.

In case of chalk the 0.2g of sample was dissolved in 1:1 nitric acid. The solution was then heated to boiling to drive off CO₂ and cooled. The sides were washed down with 20 ml of distilled water and again heated for 10 minutes. After cooling, the pH was checked and it was found that the pH was within the working range of the electrode. The solution was made up to 100 ml by adding distilled water.

In both the cases the potential was recorded using *electrode II* (Table 4.16) and the amount of calcium was calculated from the calibration curve (Fig. 4.16).

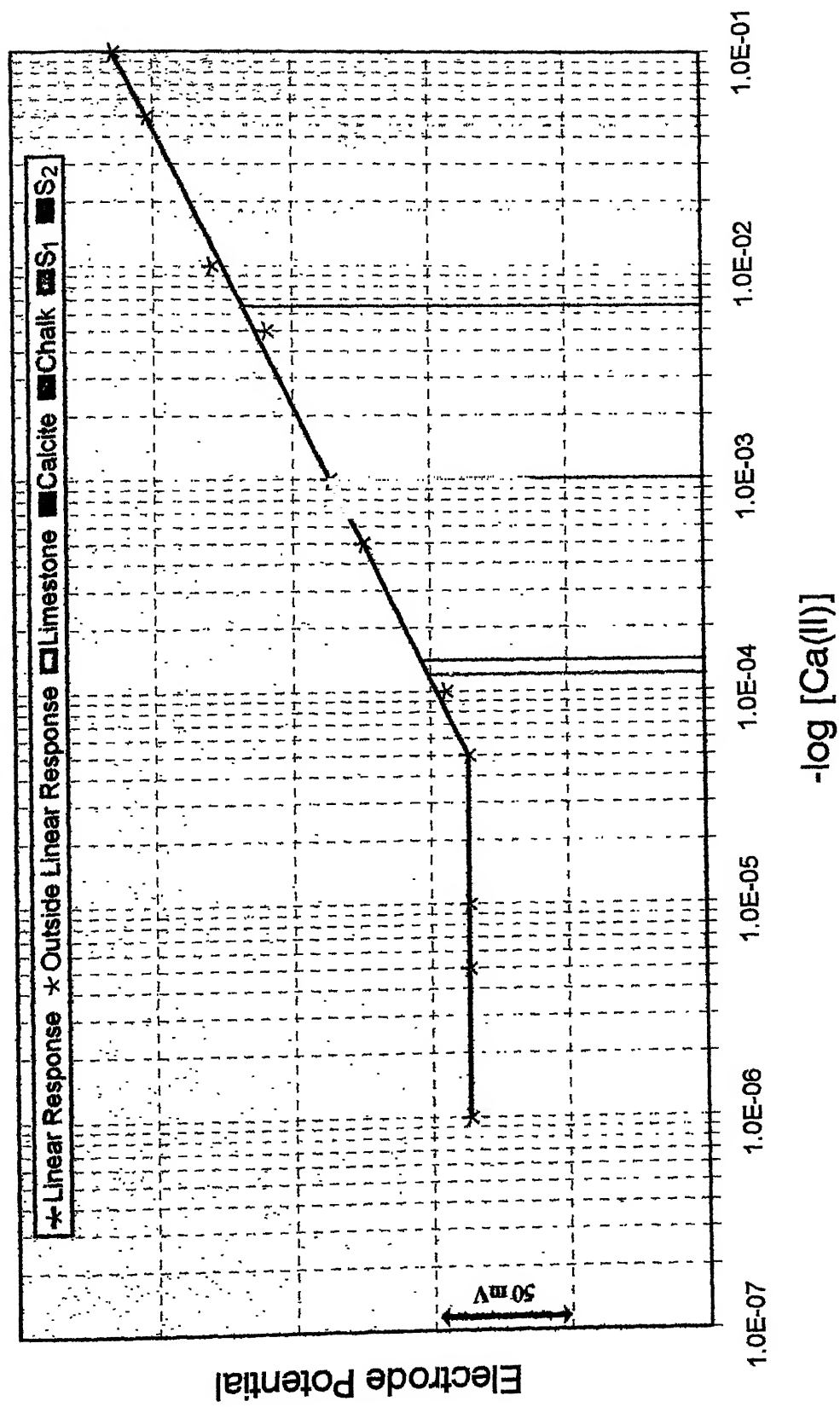
The amount of calcium was also determined at Research and Development Laboratory, IFFCO, Phulpur using AAS technique. For this the wavelength (λ_{\max}) was set at 422. 7 nm, slit at 0.7 nm and air-acetylene flame was used.

It was observed that there is a reasonable agreement between the values obtained by both the methods (Table 4.16)

Table: 4.16
Analysis of Calcite and Chalk.

Sample	Electrode Potential (mV)	Amount of Ca (II) by ISE (ppm)	Amount of Ca (II) by AAS (ppm)
Calcite	169	520	500
Chalk	137	200	200

FIG. 4.16 : Determination of Ca(II) Ion in Limestone, Calcite, Chalk and Soils



4.4.3.4 Determination of Calcium In Soils

In this section the technique for determination of calcium content in six soil samples, mentioned earlier (in chapter 2) has been described. 1.0g of each soil sample, S₁, S₂, S₃, S₄, S₅, or S₆, were taken in separate beakers and soil extract was prepared as described in chapter 2. The pH of each solution was adjusted by adding sodium acetate buffer (62) and made up to 100 ml by distilled water. The potential of each solution was recorded (Table 4.17) and converted to concentration of Ca (II) ion. The amount of Ca (II) ion present in soil was calculated from the calibration curve (Fig. 4.16).

Table: 4.17

Analysis of Soil

Soil Samples	Electrode Potential (mV)	Amount of Ca (II) by ISE (ppm)	Amount of Ca (II) by AAS (ppm)
S ₁	101	4.8	4.6
S ₂	—	—	0.9
S ₃	104	5.6	5.3
S ₄	—	—	0.5
S ₅	—	—	0.6
S ₆	—	—	0.5

The AAS technique was also used for determination of Ca (II) ion in these soils. The AAS facility was available at Research and Developments. Laboratory, IFFCO, Phulpur. The AAS was set at wavelength (λ_{max}) 422.7 nm and slit 0.7. The air- acetylene flame was used. The calcium content then recorded (Table 4.17).

The ISE method found to be not suitable when the Ca (II) concentration was very low. However at moderate concentration of Ca (II) ion in soil samples the values obtained by ISE method as well as AAS method agreed with each other.

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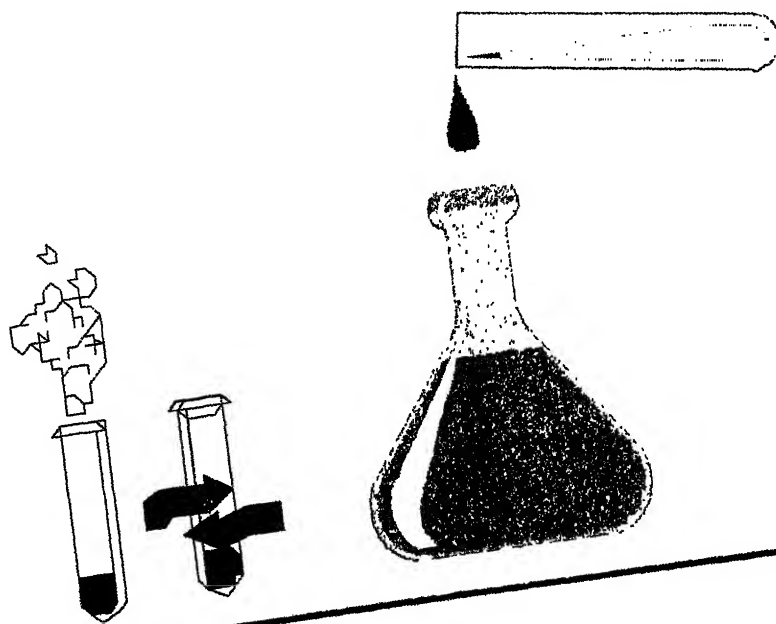
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CHAPTER 5

ISEs of Al (III), Pb (II) and their
Applications in *Bauxite, Laterite, Marl,*
Clay, Basalt, Alum, Red Lead,
Galena and Soils



ISEs OF Al (III), Pb (II) AND THEIR APPLICATIONS

5.1 INTRODUCTORY

In this chapter the fabrication as well as characteristics of some new ion selective electrodes for Al (III), Pb (II) ions and their possible application have been described. For fabrication of Al (III) ISEs three new electroactive materials, *aluminium diphenylamine*, *aluminium benzoate* and *aluminium alizarin red S* complex have been tried and for fabrication of Pb (II) ISEs two new electroactive materials *lead molybdate* and *lead diethyldithiocarbamate* have been used. The other electroactive materials used and other details of electrodes reported by different authors have been summarized in Table 5.1.

Using these fabricated electrodes an attempt was made to explore possible use of these electrodes for the analysis of Al (III) and Pb (II) ions in some naturally occurring minerals *bauxite*, *clay*, *laterite*, *marl*, *basalt*, *galena*, *red lead*, *alum* and *soil* samples.

5.2 ALUMINIUM ION SELECTIVE ELECTRODES

The preparation of electroactive materials has been described in previous chapter 3. In order to prepare electrodes with these electroactive materials three different set of membranes were prepared. In the first case, the *aluminium diphenylamine* was mixed with araldite in 1:4 ratio to make a thorough paste. In the second case *aluminium benzoate* was mixed with araldite in ratio 1:4 and in the third case the *aluminium alizarin red S* complex was mixed with araldite in 1:4 ratio. These pastes were allowed to dry to form a membrane as described in chapter 2, and electrodes prepared from these membranes were designated as *electrode I*, *electrode II* and *electrode III* respectively.

Table : 5.1**ISEs Sensitive to Aluminium and Lead**

ISE	Electroactive Material	Matrix	References
Al (III)	Al ₂ O ₃	Paraffin	1
	Aluminium Oxinate	—	2
	Aluminium dithiozonate	Epoxy resin	3
	Aluminium diphenyl amine	Epoxy resin	This work
	Aluminium benzoate	Epoxy resin	This work
	Aluminium alizarin red-S	Epoxy resin	This work
Pb(II)-	PbS (Homogeneous)	—	4
	PbS (Heterogeneous)	Silicon rubber	5
	PbS, Ag ₂ S, Cu ₂ S	—	6
	Pb- Selenide + Ag ₂ S or Pb- telluride + Ag ₂ S	—	7
	PbS + Ag ₂ S	Polyethylene	8
	PbS + Ag ₂ S+ Polythene	Thermomoulding Press	9
	Lead dithiozonate	—	10
	Bis (O', O di- isobutyl di-thiophosphato) Lead (II)	—	11
	Ag ₂ S- PbS (2:)	—	12
	Lead (II) dioxide	—	13
	Silicon grease/ Pellet agar- agar	—	14
	Pb- PbS	—	15
	Pb poly- aloxylate tetra phenyl borate	PVC	16
	Di benzo 18 Crown 6, Pb (II)	PVC	17
	Lead molybdate	Epoxy resin	This work
	Lead diethyldithiocarbamate	Epoxy resin	This work

5.2.1 Characteristics of the Electrodes

The membrane electrodes prepared as above were first conditioned for one week and then its various characteristics were studied. For the measurement of electrode potential reference solution of 0.1 mol dm^{-3} of AlCl_3 was filled inside the tube and a saturated calomel electrode was inserted inside the Al (III) ISE for electrical contact and a secondary calomel electrode was used as reference electrode. A Philips pH meter (Model PR 9405) was used for determination of potential. All experiments were carried out at room temperature ($25 \pm 2^\circ$). The electrode assembly can be represented as:



5.2.1.1 Electrode Response

In order to study the electrode response, solutions of aluminium chloride of different concentrations in the range $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ were prepared. The response of these solutions were noted for each electrode over a period of time. In case of *electrode I* it was observed that the response is linear down to the concentration of Al (III) $5 \times 10^{-4} \text{ mol dm}^{-3}$ Al (III) ion with slope 45 mV per decade change in Al (III) concentration. The response of the electrode kept changing and became stable after one month of its preparation, when it showed the linear response down to a concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$ Al (III) ion with slope 30 mV per decade change in Al (III) ion concentration (Fig. 5.1 and Table 5.2).

In the case of second electrode the response got stabilised after three weeks of its preparation when the linear response was observed down to the concentration of $5 \times 10^{-5} \text{ mol dm}^{-3}$ with slope 35 mV per decade change in Al (III) ion concentration (Fig. 5.2 Table 5.2).

While in case of third electrode the response got stabilised after three weeks, when the slope became 30 mV per decade change in Al (III) ion concentration and linear response down to 1×10^{-5} mol dm⁻³ concentration of Al (III) ion (Table 5.2 and Fig. 5.1).

Table: 5.2
Electrode Response

Concentration of Al (III) ion (mol dm ⁻³)	Electrode Potential (mV)		
	<i>Electrode I</i>	<i>Electrode II</i>	<i>Electrode III</i>
1×10^{-1}	492	350	440
5×10^{-2}	475	340	430
1×10^{-2}	435	315	415
5×10^{-3}	415	300	398
1×10^{-3}	380	280	375
5×10^{-4}	330	265	365
1×10^{-4}	315	245	355
5×10^{-5}	315	235	335
1×10^{-5}	315	235	325
5×10^{-6}	315	235	325
1×10^{-6}	315	235	325

5.2.1.2 Response Time

The response time of the electrode was determined by the method described in chapter 2. It was observed that it takes 15 seconds for *electrode I*, 20 second for *electrode II* and 25 seconds for *electrode III* to give a constant potential (Table 5.3 and Fig. 5.3).

FIG. 5.1 : Potential vs -log Concentration of Al(III) Ion

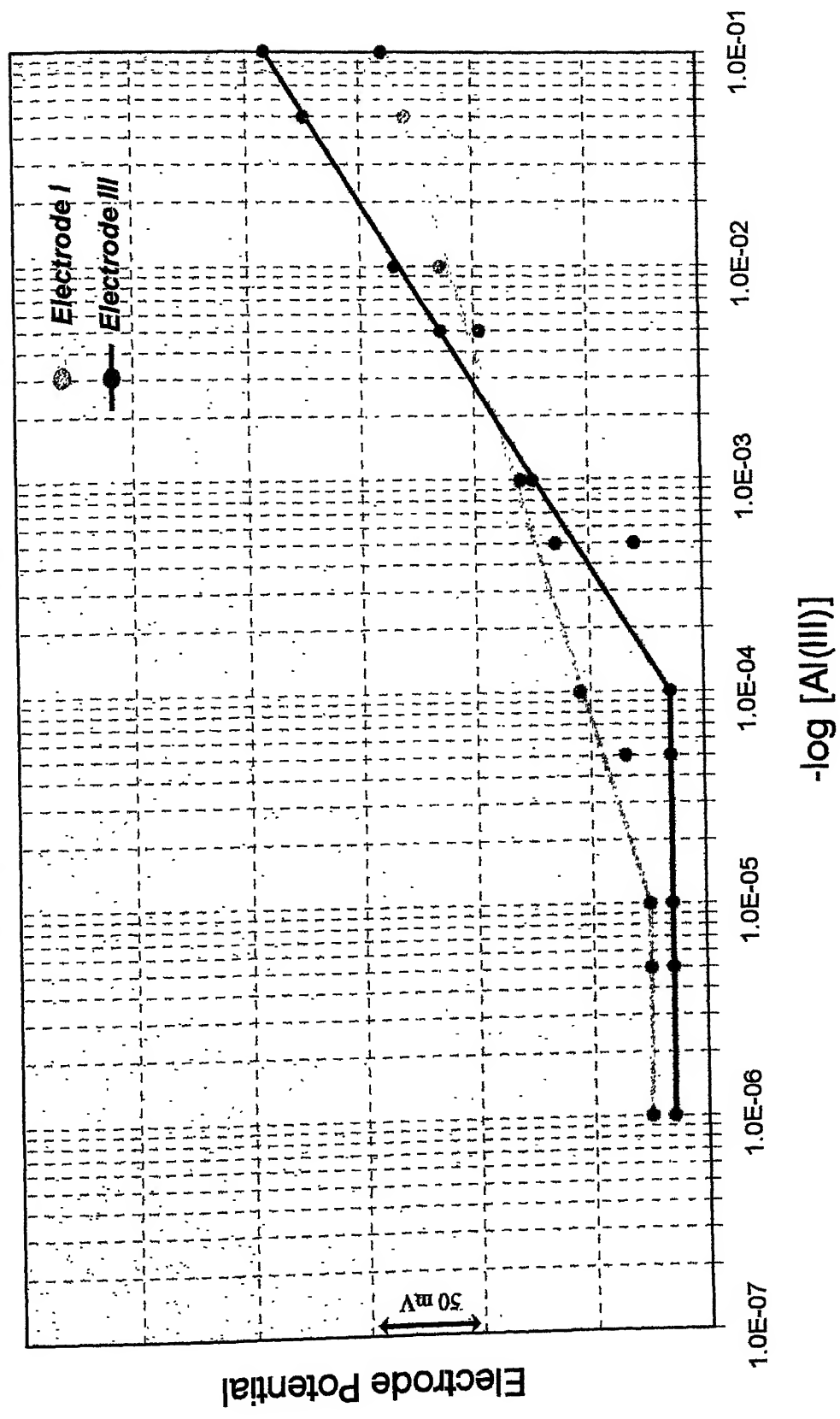


FIG. 5.2 : Potential vs-log Concentration of Al(III) Ion
in Presence and Absence of Secondary Ions

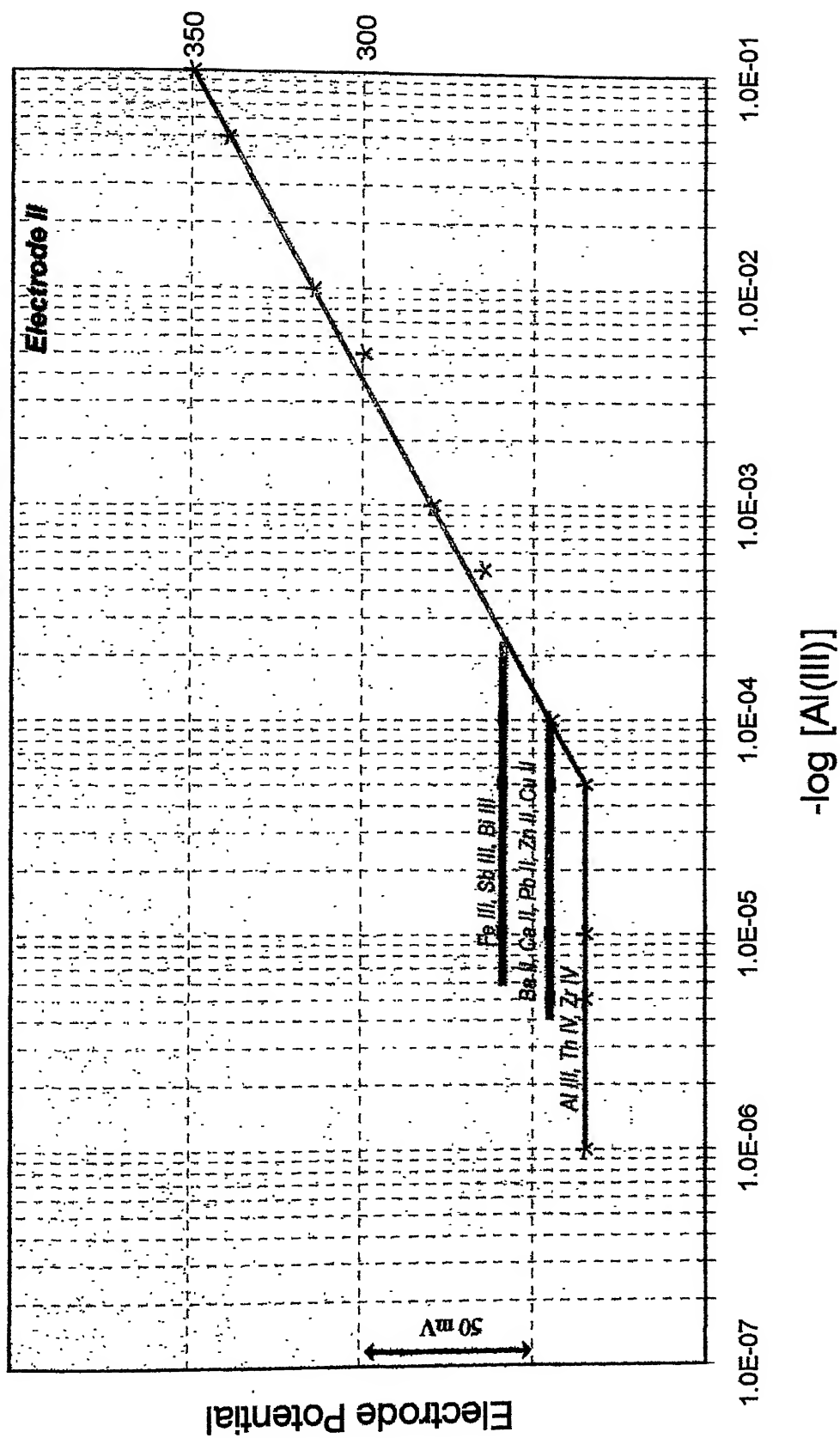


Table : 5.3**Response Time**

Time (sec)	Electrode Potential (mV)		
	<i>Electrode I</i>	<i>Electrode II</i>	<i>Electrode III</i>
0	295	315	415
5	280	300	410
10	265	295	400
15	240	290	380
20	240	280	380
25	240	280	375
30	240	280	375
35	240	280	375
40	240	280	375
45	240	280	375
50	240	280	375

5.2.1.3 Effect of pH

In order to see the effect of pH, a number of solutions with a constant concentration 0.01mol dm^{-3} of Al (III) ions but different value of pH (into range 1 to 12) were prepared. The potential of each solution for each electrode was noted (Table 5.4) and plotted against pH values (Fig. 5.4). It was observed that the potential remained constant in the range of 4 to 11 for *electrode-I*, 3 to 9 for *electrode II* and *electrode III*.

FIG. 5.3 : Potential vs Time

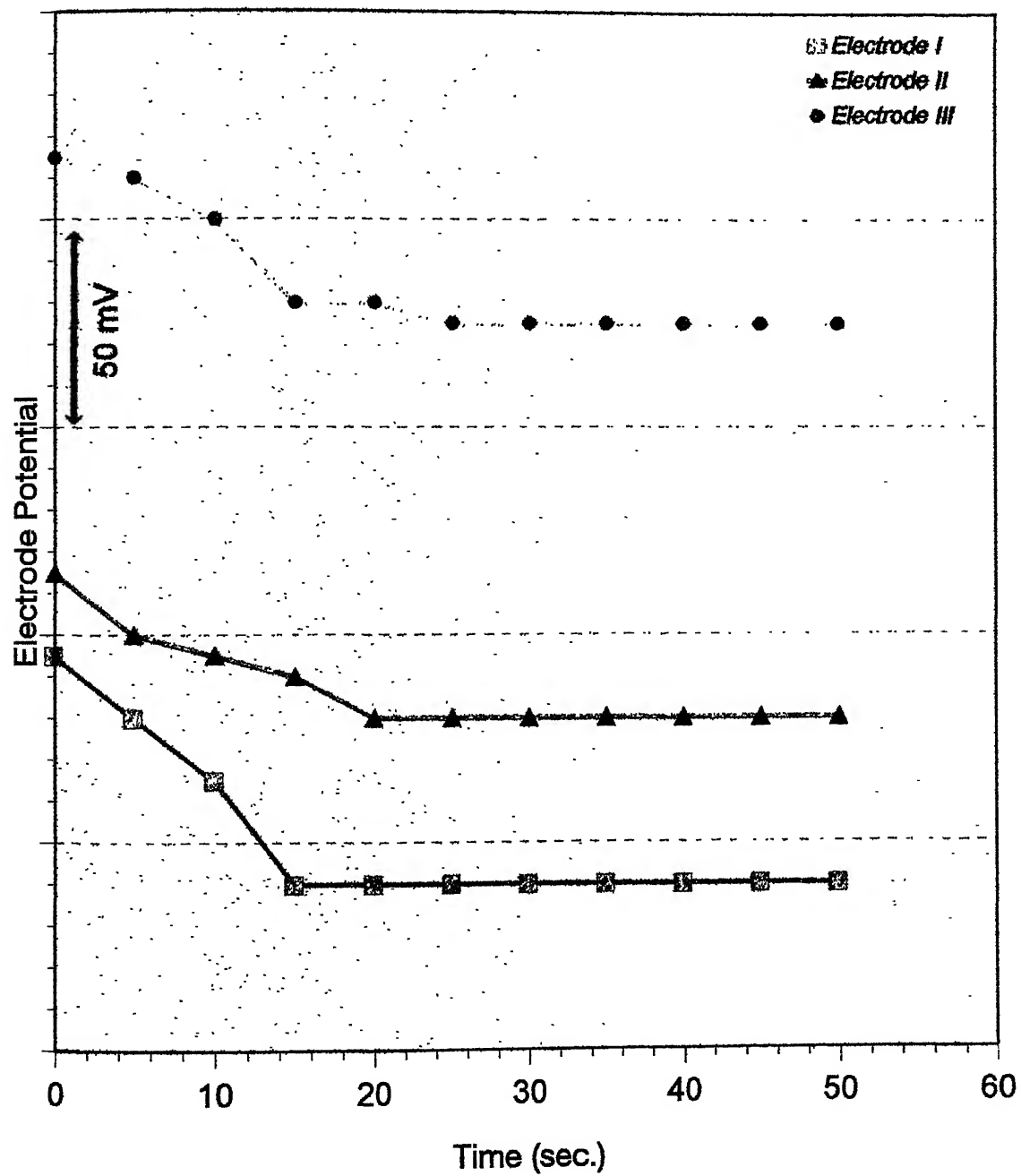


Table: 5.4
Effect of pH change

pH	Electrode Potential (mV)		
	<i>Electrode I</i>	<i>Electrode II</i>	<i>Electrode III</i>
1	298	250	200
2	255	238	175
3	245	220	155
4	225	220	150
5	225	220	155
6	225	220	155
7	225	220	153
8	225	218	155
9	225	220	155
10	225	235	180
11	225	250	185
12	240	260	190

5.2.1.4 Selectivity Coefficient

In order to assess the performance of the electrode in presence of divalent and trivalent cations, the selectivity coefficients for the electrode for different ions were determined by mixed solution method as described in of chapter 2. The values are summarized in Table 5.5 and Fig. 5.2. The electrodes were found to be selective in presence of Fe (III), Bi (II), Ba (II), Zn (II), Cu (II), Pb (II) Th (IV) and Zr (IV) ions.

5.2.1.5 Life Time

In all the three cases it was observed that after stabilization of electrode response, it remained constant upto a period of six months. Thus all the three electrodes have life time of six months approximately. After this time they show erratic behaviour.

FIG. 5.4 : Potential vs. pH

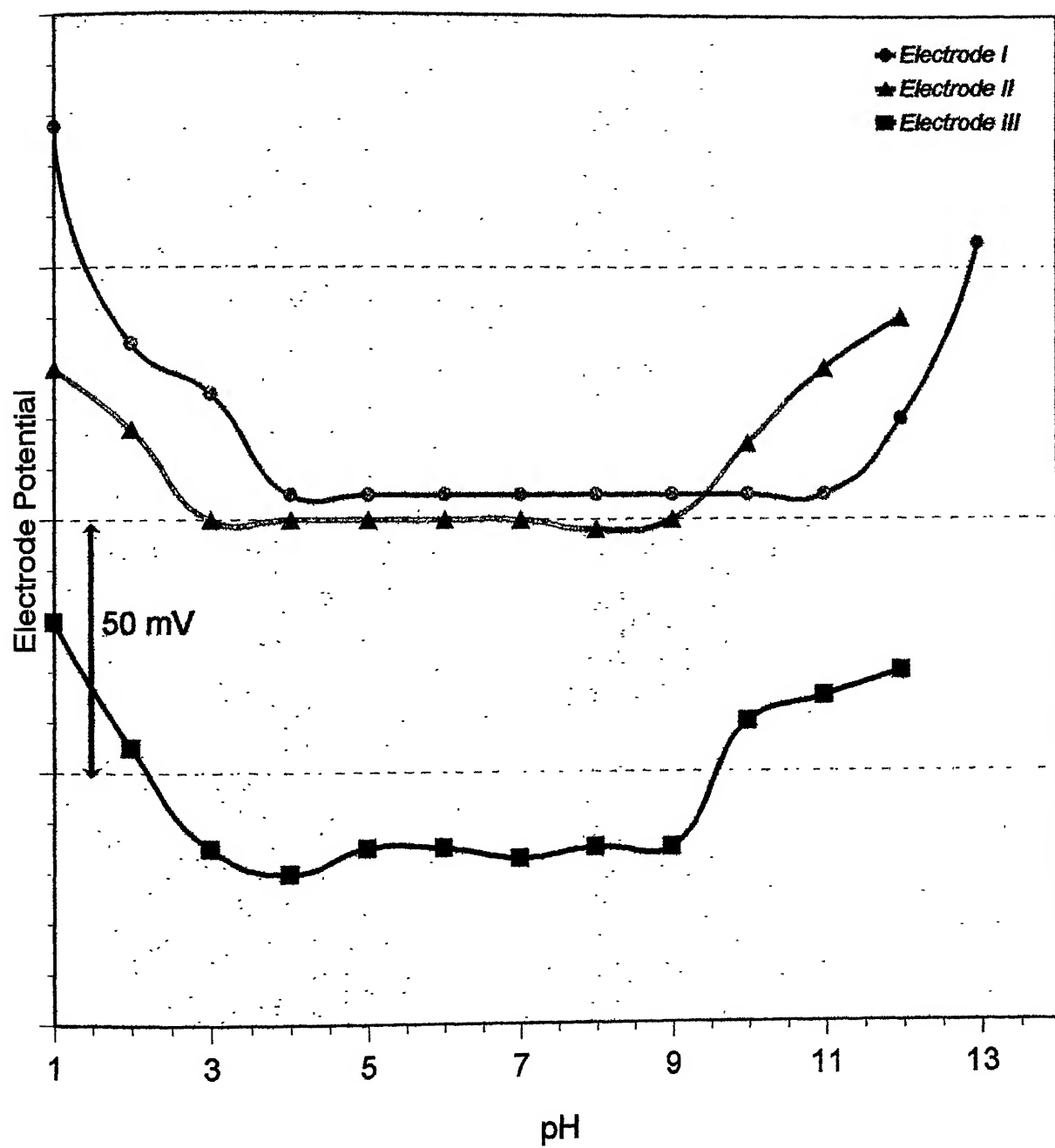


Table: 5.5
Selectivity Coefficients

Ions	$K_{Al^{3+},M}^{pot}$	Ions	$K_{Pb^{2+},M}^{pot}$
Ba (II)	0.30	Cu(II)	0.50
Ca (II)	0.30	Cd(II)	0.50
Pb (II)	0.30	Mn(II)	0.50
Zn (II)	0.30	Zn(II)	0.50
Cu (II)	0.30	Al(III)	0.01
Fe (III)	0.10	Ca(II)	0.50
Sb (III)	0.10	Co(II)	0.01
Bi (III)	0.10	Ni(II)	0.01
Zr (IV)	0.00	–	–
Th (IV)	0.00	–	–

5.2.2 Applications

To see the utility of the electrodes prepared the electrodes were used for the direct determination of Al (III) ion in different naturally occurring minerals. Aluminium as an element constituting about 7 percent of earth, and as the most abundant metal, it follows that aluminium is present in many samples. Aluminium ion is colourless and forms no coloured inorganic compounds of low solubility. Therefore, methods of its determination are limited to salts of high molecular weight organic acids, which are usually dyestuffs. Since the reagent as well as its aluminum lake is coloured, the photometry can be applied.

In the present work, attempts has been made to determine the aluminum ion concentration in samples by ISE method. The ISE was successfully used in the analysis of rocks, ores, soils, and different other minerals (18-21). For this some naturally occurring minerals

such as *bauxite*, *clay*, *laterite*, *basalt*, *alum* and *marl* have been studied.

5.2.2.1 Determination of Aluminium in Bauxites

In order to determination the aluminium content in bauxite samples, two sets of bauxite samples were taken with respective weights as 0.2g and 0.5g. in separate beakers. Each of two sets of samples, thus weighed for bauxite A, bauxite B and bauxite C were dried at 100°C. A solution consisting at the mixture of nitric, hydrochloric and sulphuric acids were prepared by taking 100 ml of concentrated nitric, 300 ml of concentrated hydrochloric and 600 ml of concentrated sulphuric acids (22). Now each of the bauxite sample was treated with 20 ml of acid mixture and was boiled and evaporated until white fumes were evolved. After evolution of white fumes the heating of mixtures were continued for 15 minutes. Solutions were then cooled and 10ml of distilled water was added in each solution followed by stirring and boiled again for 10 minutes. By this method the silica got precipitated and was separated by filtration. The volume of filtrates were made up to 100 ml by adding distilled water. The pH of each sample solution was adjusted within the working range of electrode by dil NaOH. Then potential of each solution was measured with the help of above prepared *electrode I* (Table 5.6). From Calibration curve the potential of each solution was converted into concentration of Al (III) ion. (Fig. 5.5).

The amount of Al (III) was also determined by XRF by courtesy of Saurashtra Cement Factory, Gujrat and the values thus obtained are compared the values obtained by ISE method (Table 5.6). There is a fairly good agreement between values obtained by XRF analysis and ISE technique in all the sets of bauxite samples.

Table 5.6

Analysis of Bauxite A, Bauxite B and Bauxite C

Sample	Weighted Amount of Sample (g)	Electrode Potential (mV)	Amount of Al (III) by ISE (g)	Amount Al (III) by XRF (g)
Bauxite A	0.2	281	0.0540	0.0575
	0.5	298	0.1350	0.1437
Bauxite B	0.2	284	0.6480	0.0620
	0.5	299	0.1485	0.1549
Bauxite C	0.2	286	0.0702	0.0674
	0.5	301	0.1620	0.1685

5.2.2.2 Determination of Aluminum in Clay, Laterite, Basalt and Marl

Clay is a heterogeneous mixture of several different minerals, the mineral *Kaolinite* with empirical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ is considered to be clay (23). For analysis, besides *Kaolinite*, the other minerals those were taken for determination of aluminium ion are *laterite*, *basalt* and *marl*.

0.2g, 0.5g and 1.0g of laterite and basalt, 0.5g and 1.0g of clay, 2.0g and 3.0g of marl samples as described in chapter 2, were taken in respective beakers. Now 2 ml of 1:1 sulphuric acid and 5 ml of concentrated hydrofluoric acid was added in each beaker. All the beakers were heated on hot plate to copious fumes and then cooled. After cooling the beakers were washed down the sides with about 10 ml of distilled water and again evaporated to copious fumes. All the beakers were cooled and about 20ml of distilled water was added after checking the pH. If the pH was found to be outside the working pH range of electrode, then it was brought up to the working range by adding dil NaOH solution.

FIG. 5.5 : Determination of Al (III) Ion in Bauxite A, Bauxite B and Bauxite C Samples

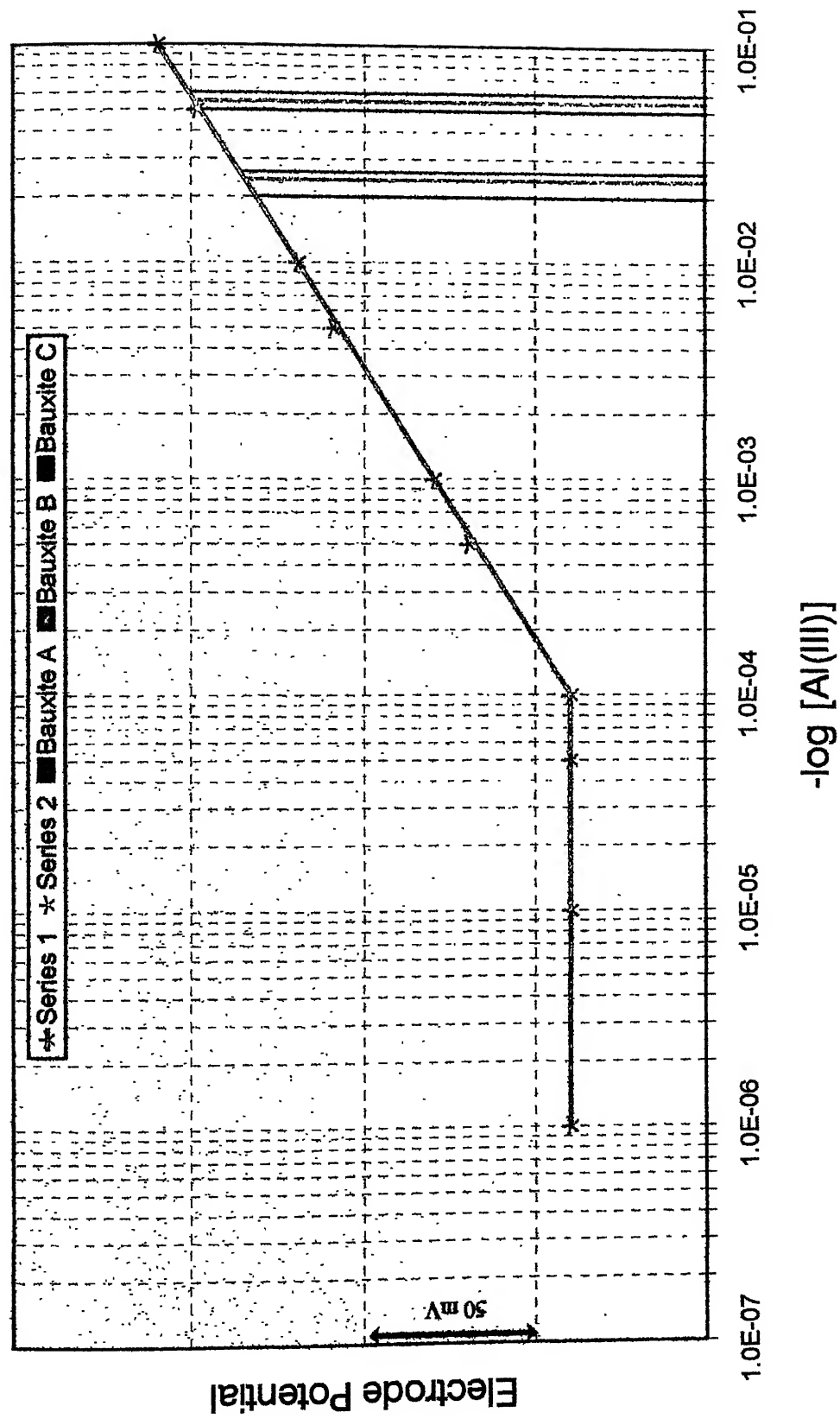


FIG. 5.6 : Determination of Al (III) Ion in Clay, Marl and Alum

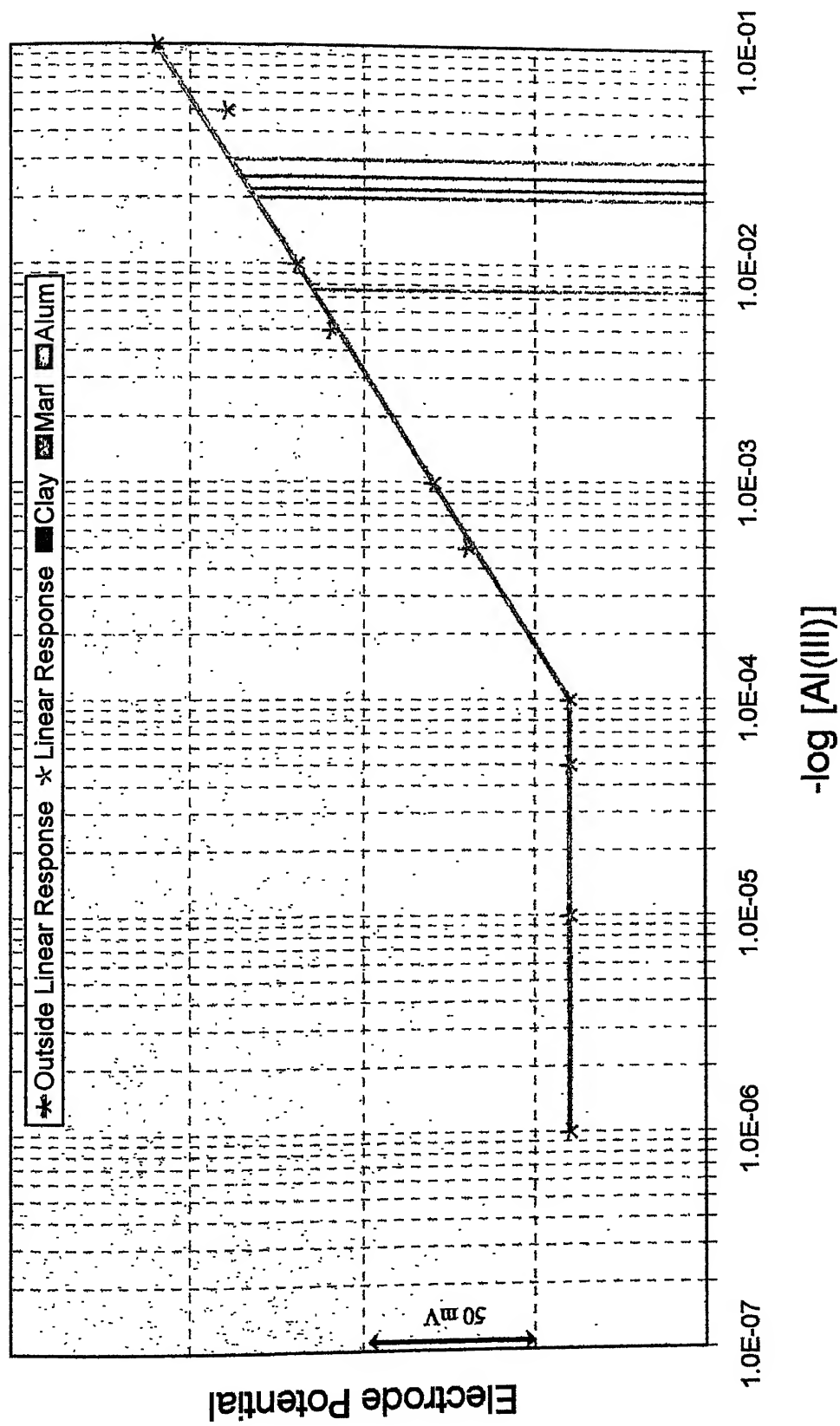
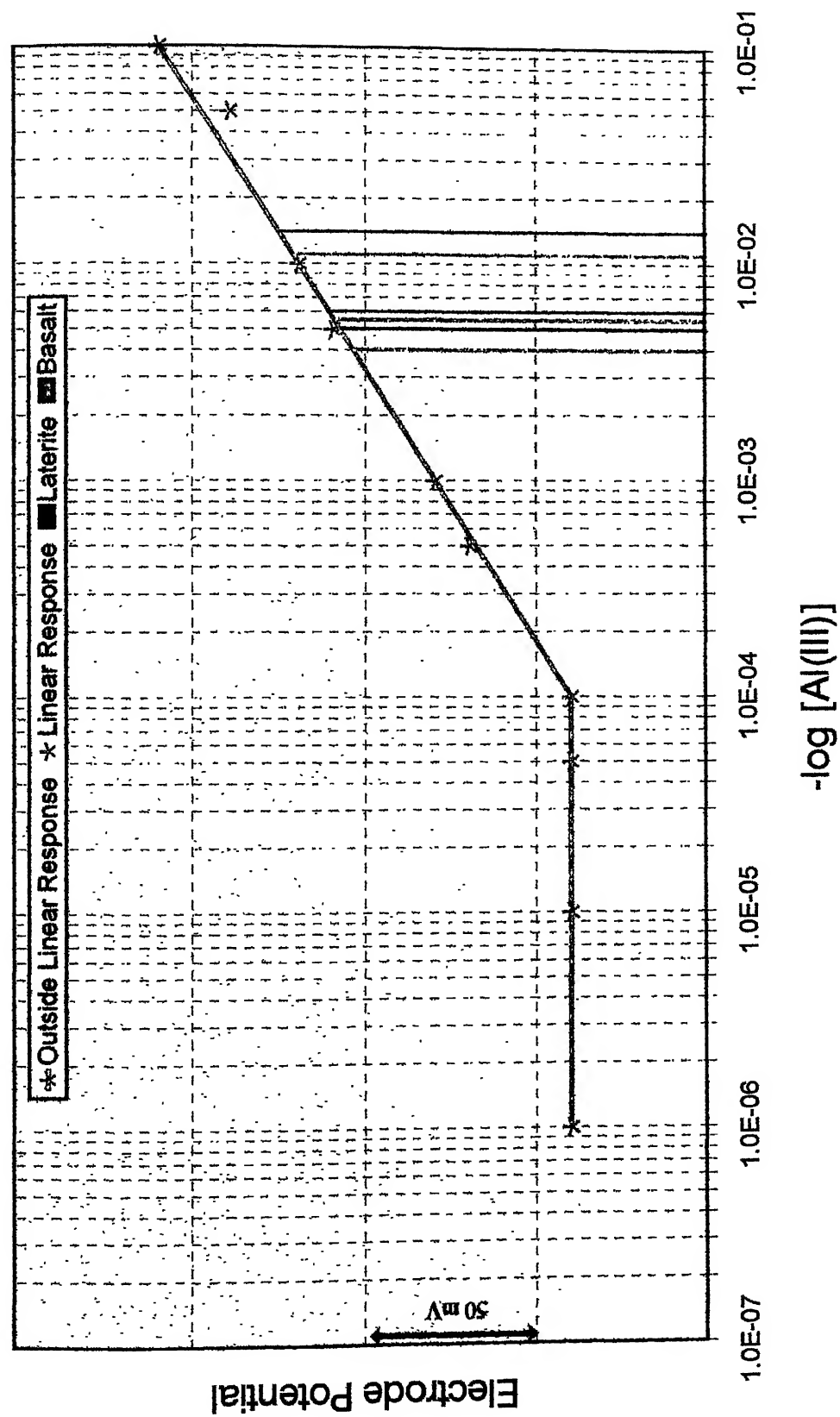


FIG. 5.7 : Determination of Al (III) Ion in Laterite and Basalt



Then solutions were transferred to 50 ml or 100ml volumetric flasks and final volume was made up to 50 ml or 100ml as the case may be. The potentials of each solution was recorded (Table 5.7) and the aluminium content in samples were calculated by calibration curve. (Fig. 5.6 and 5.7).

The aluminium content of each sample was also determined by XRF method by the courtesy of Saurashtra Cement Factory Gujrat (Table 5.7).

There is a reasonable agreement between the values obtained from ISE method with the values obtained by XRF method.

Table : 5.7

Analysis of Clay, Laterite, Basalt, and Marl

Sample	Weighted Amount of Sample (g)	Volume (ml)	Electrode Potential (mV)	Amount of Al (III) by ISE (g)	Amount of Al(III) by XRF (g)
Laterite	0.2	50	257	0.0068	0.0077
	0.5	100	260	0.0162	0.0192
	1.0	100	275	0.0336	0.0384
Basalt	0.2	50	254	0.0054	0.006
	0.5	100	259	0.0148	0.015
	1.0	100	271	0.0298	0.030
Clay	0.5	50	283	0.0338	0.0135
	1.0	100	286	0.0674	0.063
Marl	2.0	100	282	0.0540	0.0578
	3.0	100	289	0.0810	0.0868

5.2.2.3 Determination of Aluminium In Alum

When a mixture of potassium sulphate and aluminium sulphate was dissolved in water and concentrated, a double salt separates in the form of crystals. The composition of the double salt corresponds to formula $KAl(SO_4)_2 \cdot 12H_2O$. All the double sulphates with similar composition and properties are called alums.

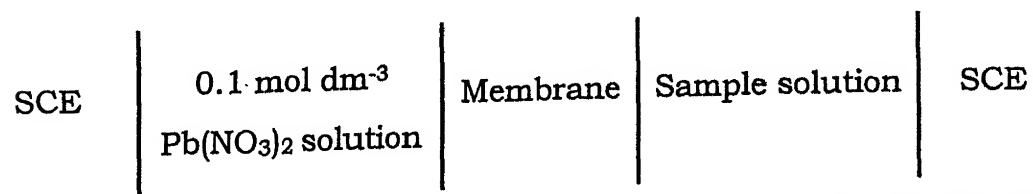
Alum is generally used in purification of water, as a mordant in dyeing, for tanning of leather, for sizing of paper and as a styptic to arrest bleeding

In the present work common alum, "potash alum", $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (B.D.H.) was used for determination of aluminium ion. 0.2 g of alum was weighed and was dissolved in distilled water. The pH of the solution was checked and it was found that the pH was within the working range of the electrode. Then the volume was made up to 50ml. The potential of solution was recorded 265 mV and the quantity of Al(III) was worked out from the calibration curve (Fig. 5.6) as 0.0106 g, where as, the value of Al (III) present in the potash alum is 0.0114 g Thus, we see the agreement between the standard value and experimentally determined value.

5.3 LEAD ION SELECTIVE ELECTRODE

For the fabrication of Pb(II) ISEs two different electroactive materials were used, methods of preparation of which are given in chapter 3. The electrode prepared from *lead molybdate* was designated *electrode I* and which was prepared from *lead diethyldithiocarbamate* was *electrode II*. First the master membrane was prepared using the electroactive materials and epoxy resin as described in chapter 2. From these master membranes two different electrodes were prepared in which the internal solution was $\text{Pb}(\text{NO}_3)_2$ and internal reference was saturated calomel electrode.

The electrode assembly can be represented as:



Before making measurement the electrode assembly was dipped in 0.01 mol dm^{-3} solution of Pb(II) ion for 10 days. The Philips pH-

meter (PR 9405) was used for measurements. All the measurements were carried out at room temperature ($25 \pm 2^\circ$).

5.3.1 Characteristics of the Electrodes

After conditioning the following characteristics of both the electrodes were studied.

5.3.1.1 Electrode Response

In order to measure the electrode response solutions of different concentrations of Pb (II) ions were prepared in the concentration range from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$. Using both the electrodes one by one the electrode potential of each solution was recorded.

The values are given in Table 5.8 from which the graph were constructed (Fig. 5.8) and we find that the *electrode I* gives a linear response down to a concentration of Pb (II) ion $5 \times 10^{-5} \text{ mol dm}^{-3}$ with a slope value 35 mV pre decade change in Pb(II) ion concentration.

Table: 5.8
Linear Response

Concentration of Pb(II) ion (mol dm^{-3})	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
1×10^{-1}	258	256
5×10^{-2}	247	248
1×10^{-2}	222	228
5×10^{-3}	210	215
1×10^{-3}	180	200
5×10^{-4}	162	195
1×10^{-4}	152	170
5×10^{-5}	142	163
1×10^{-5}	142	145
5×10^{-6}	142	145
1×10^{-6}	142	145

FIG. 5.8 : Potential vs $-\log$ Concentration of Pb(II) Ion
in Presence and Absence of Secondary Ions

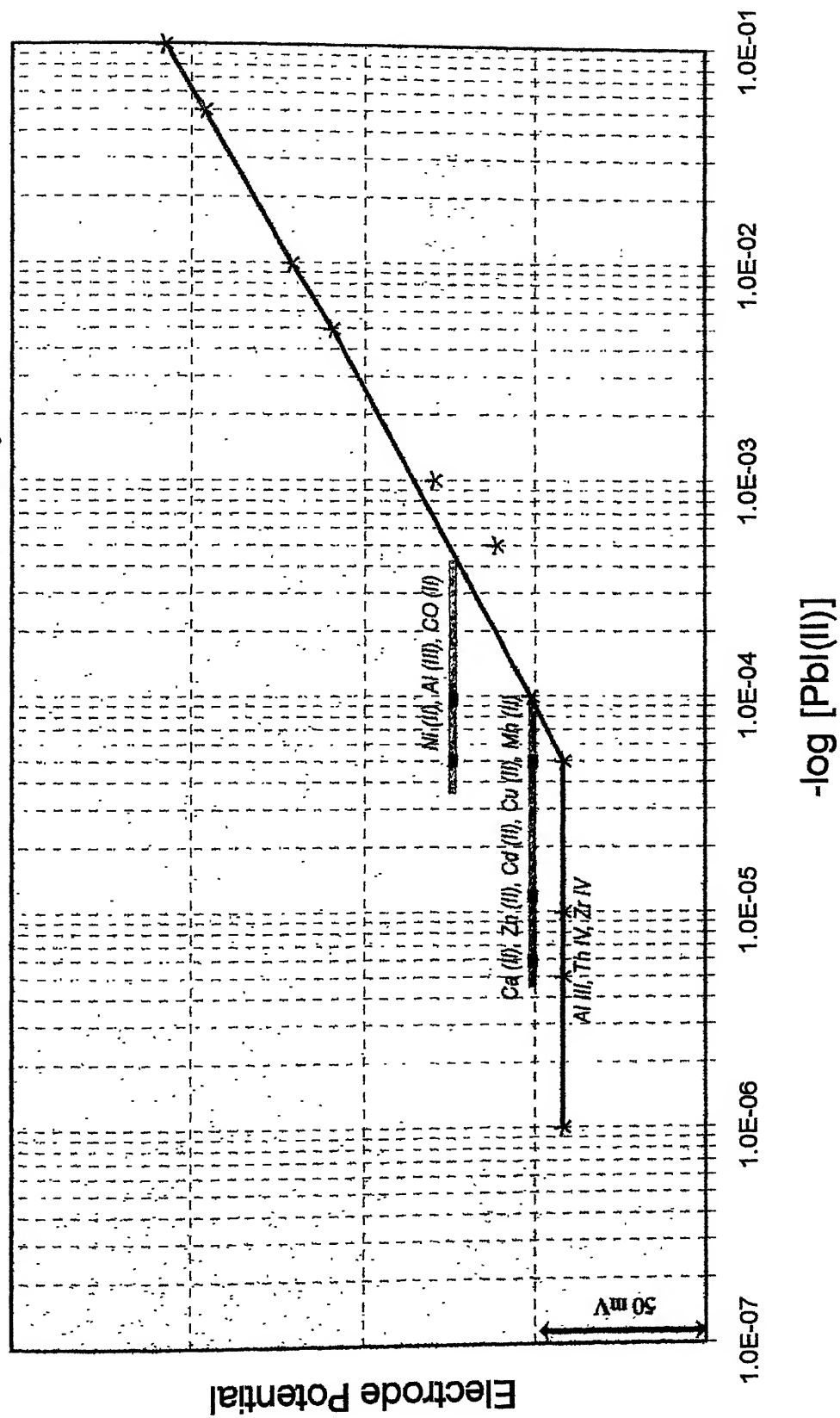
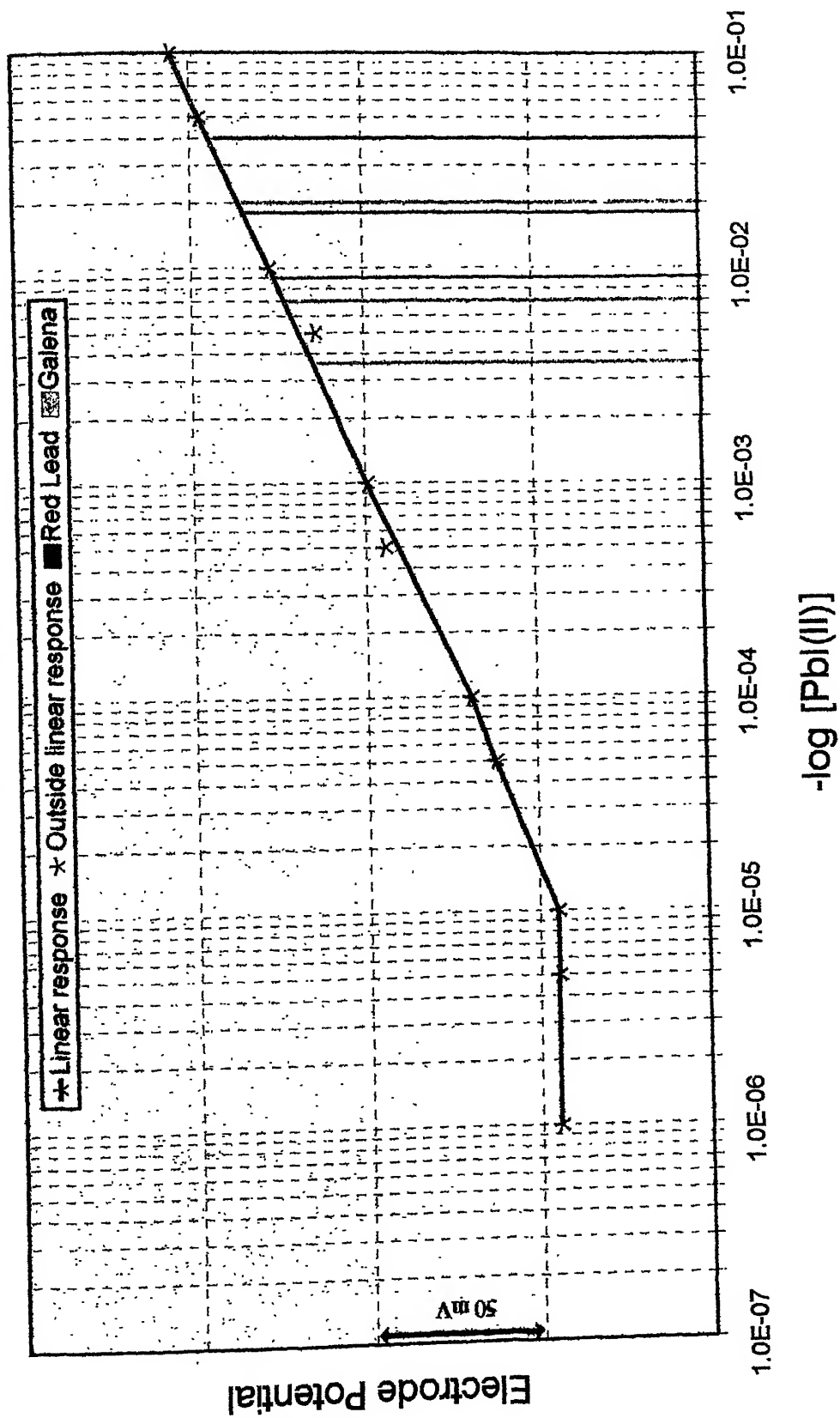


FIG. 5.9 : Potential vs $-\log$ Concentration of Pb(II) Ion and Determination of Pb(II) Ion in Galena and Red Lead



The linear response for *electrode II* was down to concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$ Pb (II) ion with a slope 28 mV per decade change in Pb(II) ion concentration (Fig. 5.9).

5.3.1.2 Response Time

In order to find the response time of the electrodes the electrode assembly was first dipped in $1 \times 10^{-1} \text{ mol dm}^{-3}$ solution of the Pb(II) ion and when the solution concentration was changed to $1 \times 10^{-2} \text{ mol dm}^{-3}$ the response of each electrode was recorded at every 5 seconds interval Table 5.9. The potentials were then plotted against time (Fig. 5.10) and it was found that the response time for *electrode I* was 30 seconds and 25 seconds for *electrode II*.

5.3.1.3 Effect of pH

A set of Pb (II) ions were prepared in which Pb(II) ion concentration was kept constant as $1 \times 10^{-2} \text{ mol dm}^{-3}$ and the pH of these solutions was varied in the range 1 to 9. The electrode potential of each solution for both the electrodes were recorded (Table 5.10) and the values were plotted against pH (Fig. 5.11). It was found that in the pH range 2 to 6 the electrode potential remains constant for both the electrodes. Thus making it a working pH range for both the electrodes.

5.3.1.4 Selectivity Coefficient

The selectivity coefficient for both the electrodes were determined by mixed solution method. For this the concentration of Pb(II) ion was varied while the concentration of interfering ion was kept constant at $1 \times 10^{-3} \text{ mol dm}^{-3}$. Then the potentials for each solutions were noted and plotted on a semi log graph paper (Fig. 5.8). The selectivity coefficients were then calculated (Table 5.5.) It was found that Pb(II) ISEs were selective in presence of Cu (II), Cd (II), Mn(II), Zn (II), Ca(II), Ni (II), Co (II) and Al (III) ions.

5.3.1.5 Life Time

It was observed that, initially the value of electrode potentials for both the electrodes kept varying with time but got stabilised after 10 days and became constant up to six months. Therefore, the life time of both electrodes are six months and after this time the electrodes show erratic behavior.

Table: 5.9
Response Time

Time (sec)	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0	222	200
5	210	190
10	203	185
15	195	175
20	190	170
25	185	165
30	180	165
35	180	165
40	180	165
45	180	165
50	180	165

Table: 5.10
Effect of pH

pH	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
1	295	263
2	240	255
3	241	255
4	241	258
5	241	255
6	240	254
7	—	270

FIG. 5.10 : Potential vs. Time

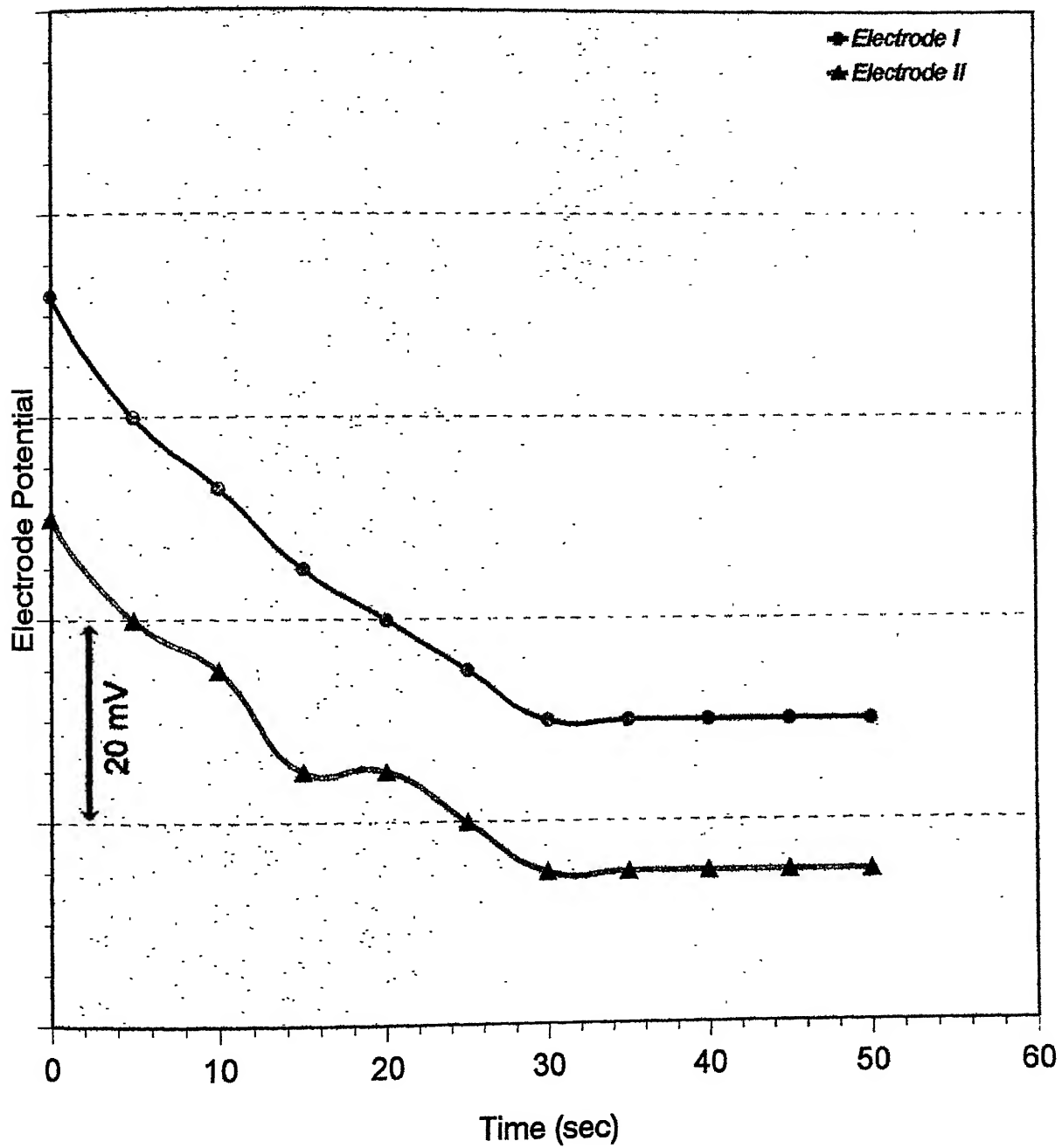
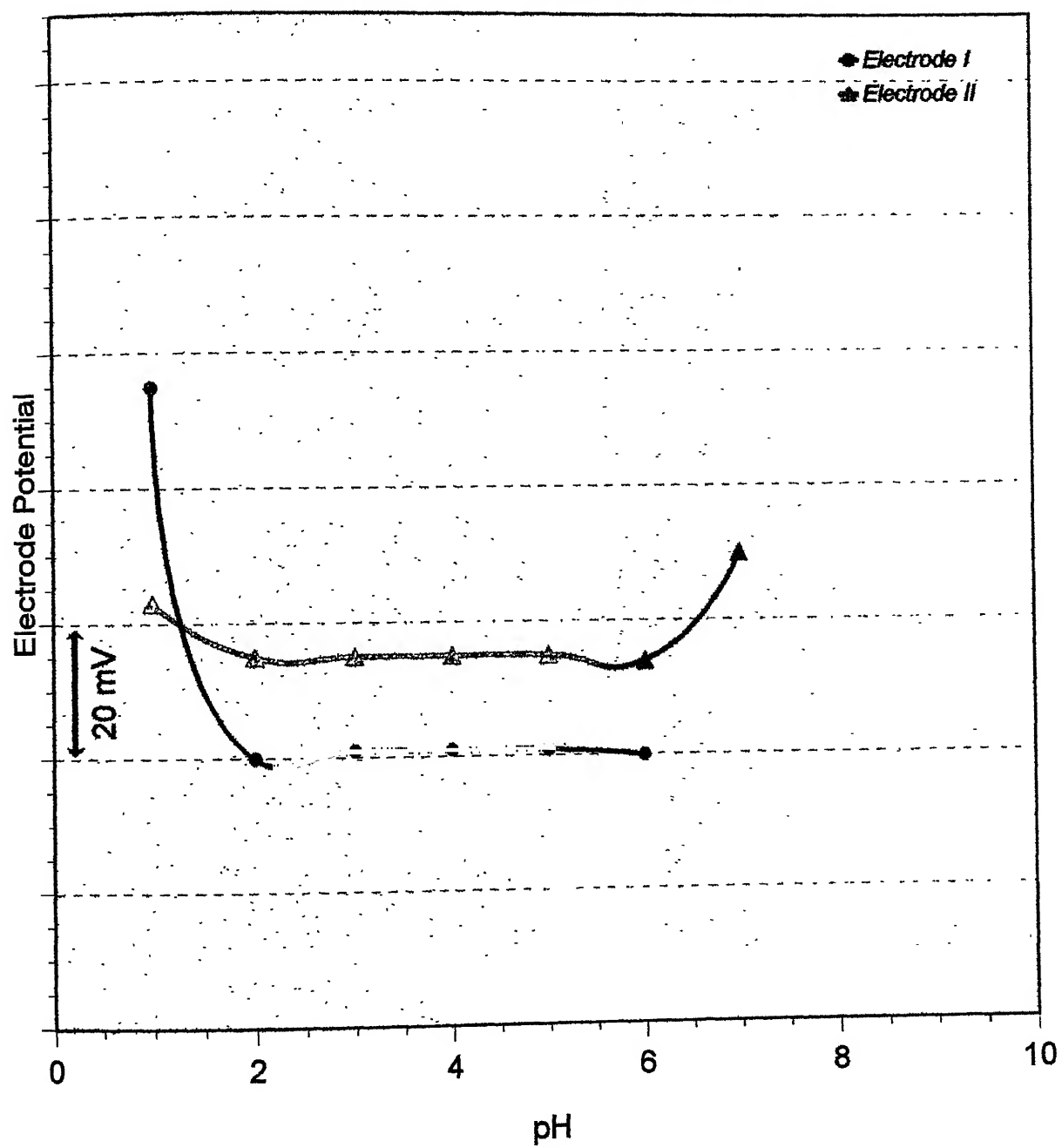


FIG. 5.11 : Potential vs. pH



5.3.2 Applications

A number of authors have previously tried to use their Pb (II)ISE for following the precipitation titration (24-27). The application of Pb(II) ISE in the direct analysis of sample solution has been also attempted (28-33).

To see the utility of the electrodes prepared, the electrodes were used as an indicator electrode in the precipitation titration and also used in the direct determination of lead ion in naturally occurring minerals and soil samples.

5.3.2.1 Titration of Lead Nitrate against Potassium Chromate

The lead (II) ISEs could be used as an indicator electrode in the precipitation titration of 0.01 mol dm^{-3} Pb (NO₃)₂ against 0.01 mol dm^{-3} K₂CrO₄. For this 5 ml of lead nitrate was taken in a flask and the potential change was noted after each addition of a small volume of a titrant added from the microburette (Table 5.11). Then the electrode potentials to be observed were plotted against the volume of titrant consumed (Fig. 5.12). An inflexion point occurs in the graph near the equivalence point of the titration.

5.3.2.2 Determination of Lead in Galena

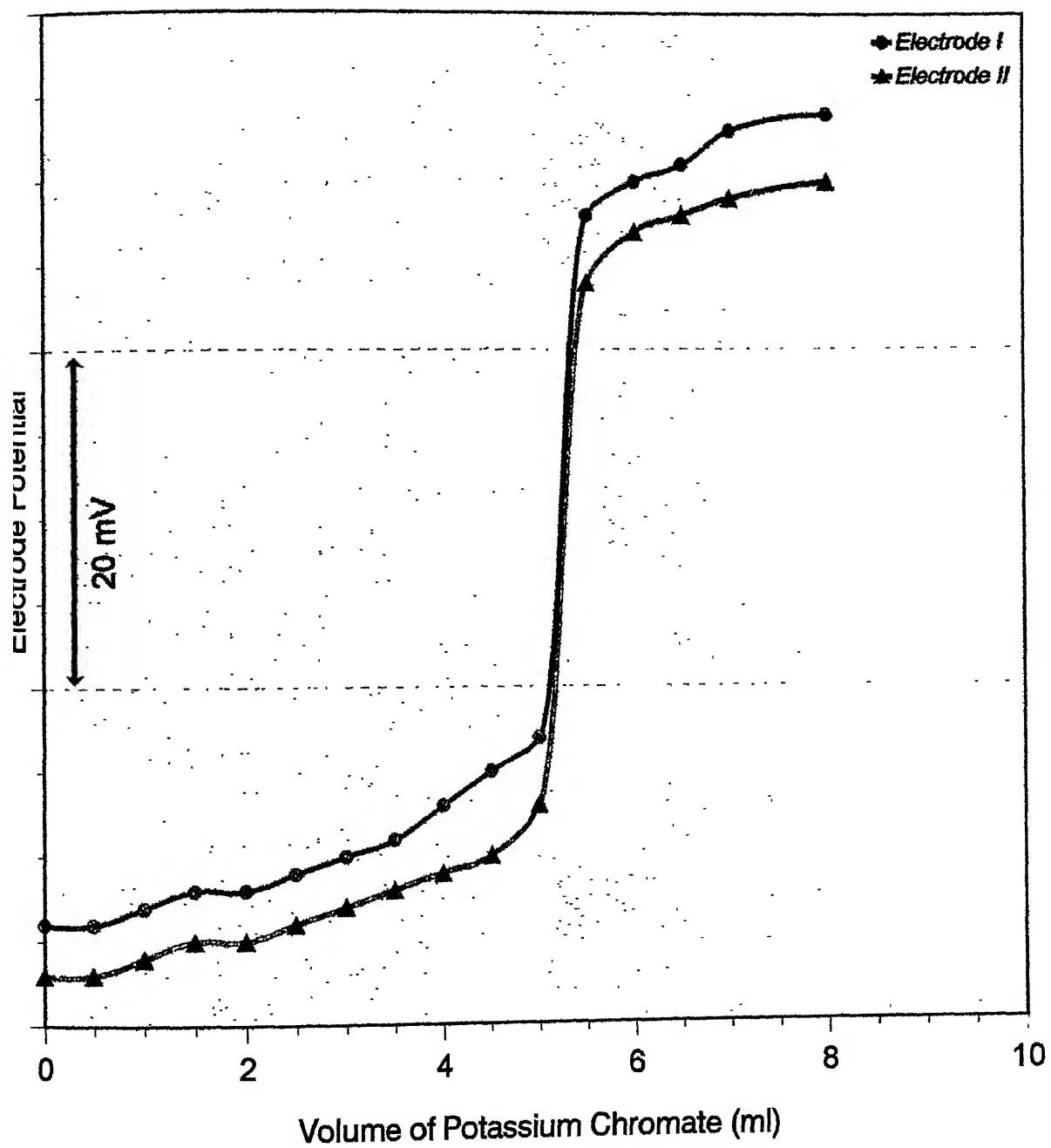
Galena may be accompanied by products of the decomposition of lead sulphide, anglesite and cerussite-quartz, silicates, blende, calcite, fluorospar, heavy spar and pyrites. Certain varieties also contain arsenic and antimony; and argenti ferrous galena may contain upto 1.0 percent of silver.

Table: 5.11**Titration of Lead Nitrate against Potassium Chromate**

Volume of Titrant (ml)	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0.0	56	53
0.5	56	53
1.0	57	54
1.5	58	55
2.0	58	55
2.5	59	56
3.0	60	57
3.5	61	58
4.0	63	59
4.5	65	60
5.0	67	63
5.5	98	94
6.0	100	97
6.5	101	98
7.0	103	99
8.0	104	100

For determination of lead in galena 0.1g, 0.2g and 0.5g powdered sample was taken in separate beakers and heated with 5 ml (1:1) sulphuric and 1.5 ml of concentrated hydrofluoric acids on a sand bath at 200-250°C and heating continued until fumes of SO₂ were given off. Now 5 drops of nitric acid was added and again heated until SO₂ fumes were given off. 25 ml of distilled water was added in each beaker and heated to boiling for few minutes until a clear

FIG. 5.12 : Titration of Lead Nitrate vs. Potassium Chromate



solution was obtained. pH was adjusted to 3-4 by adding dil NaOH. Then the solutions were made up to 100 ml by adding distilled water and potential was noted using *electrode II* in each case (Table 5.12). The amount of lead present in galena was calculated from the calibration curve (Fig. 5.9) In order to compare the value of Pb(II) ion in galena determined by ISE method, the lead content of sample was also determined by AAS technique. The work was carried out by AAS at the Research and Development Laboratory, IFFCO, Phulpur. For this the instrument was set as wavelength was 283.3 nm, slit was 0.7 nm and air-acetylene flame was used.

Table: 5.12

Analysis of Galena

Weighed Amount of Sample (g)	Electrode Potential (mV)	Amount of Pb (II) by ISE (g)	Amount of Pb (II) by AAS (g)
0.1	214	0.0746	0.0782
0.2	223	0.1450	0.1564
0.5	235	0.4144	0.3910

Comparing these values we find that there is a reasonable agreement between the values obtained by both the techniques.

5.3.2.3 Determination of Lead In Red lead

Red lead is made by usually by roasting "pig lead" until the oxidation ceases makes red lead. The red lead may contain as impurities or adulterants heavy spar, lead sulphate, silica, ferric oxide, copper oxide and bismuth oxide. It also contains metallic lead and various lead oxides PbO, Pb₂O₃, PbO₂. Silica and clay may be derived from the floor of the muffle in which the red lead was roasted.

In order to determine Pb(II) ion in red lead 0.1 g, 0.2 g and 0.5 g of red lead was taken in different beakers and few drops of 10 % acetic acid was added. The dissolution was greatly facilitated by the addition of about 10 ml hydrogen peroxide (5 %) just after the addition of acetic acid. The solutions were heated for about an hour on hot plate. Then it was filtered and washed with hot distilled water. The insoluble residue contains clay, silica and heavy spar-barium sulphate. The filtrate was made up to 50 ml by distilled water after adjusting the pH within working range of working range of electrode by dil NaOH. The potential was recorded for each solution using *electrode II* and the amount of lead was calculated from the calibration curve (Table 5.13 and Fig. 5.9).

Table : 5.13

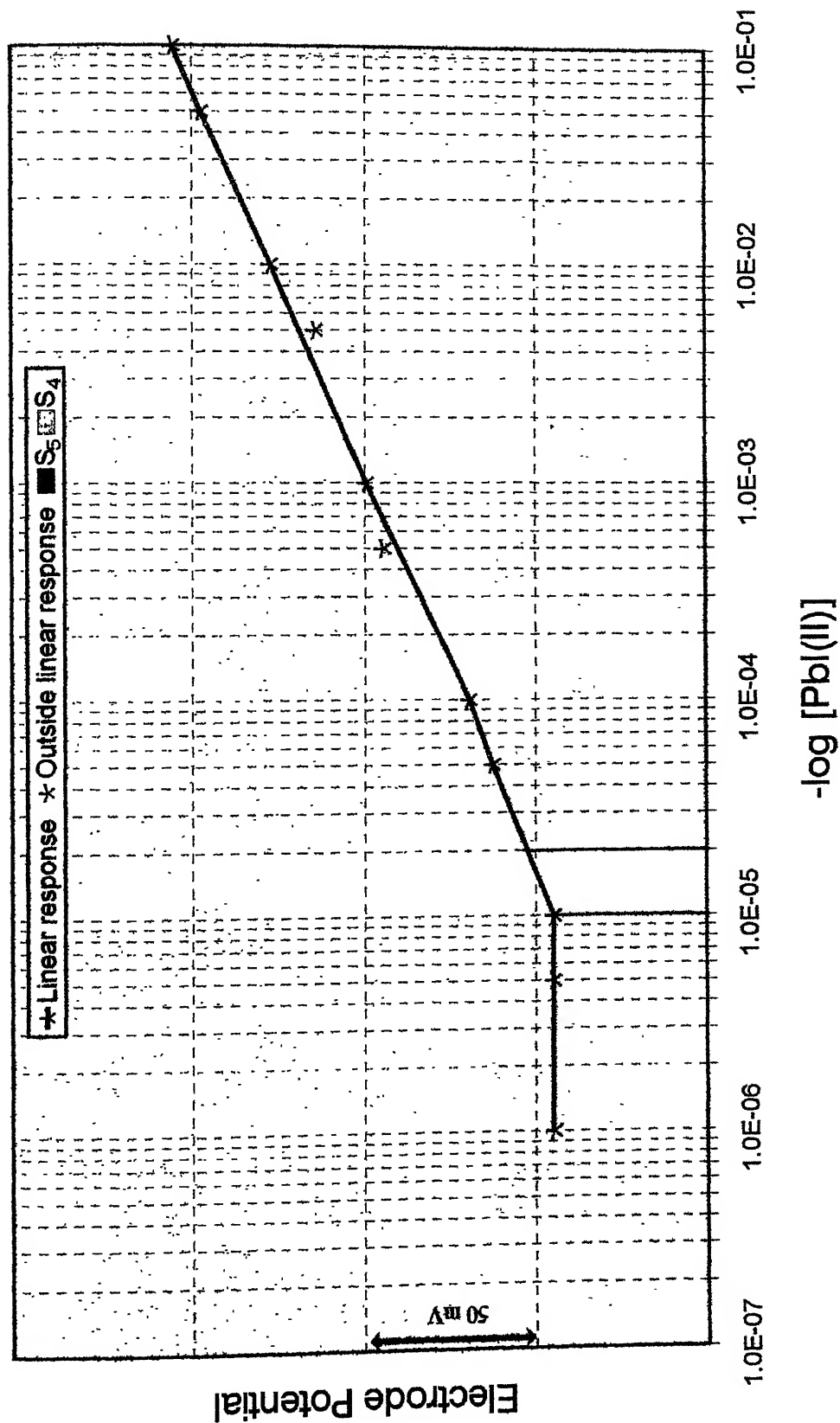
Analysis of Red Lead

Weiighed Amount of Sample (g)	Electrode Potential (mV)	Amount Pb (II) by ISE (g)	Real Values (g)
0.1	226	0.0906	0.0932
0.2	234	0.1812	0.1864
0.5	243	0.4532	0.4144

5.3.2.4 Determination of Lead in Soils

For determination of lead in soils 1.0g of each soil S₁, S₂, S₃, S₄, S₅ or S₆ as described in chapter 2, was taken in separate beakers. Soil extract was prepared by using the method described in chapter 2. After preparing the extract, pH of all the soil solutions were recorded and it was found that the pH was within the working range of the electrode. Now the potential of all the sample solutions were recorded by using the Pb(II) ISE and value of lead in samples were calculated by the help of calibration curve (Table 5.14 and Fig. 5.13). For the

FIG. 5.13 : Determination of Pb(II) Ion in Soil Samples



determination of lead content in soils the AAS technique was also used. The study was carried out at Research and Development Laboratory IFFCO, Phulpur. The AAS was set at wavelength (λ_{\max}) 283.3 nm, slit 0.7nm and flame air-acetylene was used . The value of lead content was then recorded (Table 5.14) and it was observed that there is a good agreement between the values obtained by ISE method.

However, when the lead content in the sample was less than 0.1 ppm the amount of Pb (II) ion can not be determined by ISE method.

Table : 5.14

Analysis of Soils

Sample	Electrode Potential (mV)	Amount of Pb(II) by AAS (ppm)	Amount of Pb(II) by ISE (ppm)
S ₁	—	0.0	0.0
S ₂	—	0.1	—
S ₃	—	0.1	—
S ₄	145	0.3	0.312
S ₅	154	0.8	0.829
S ₆	—	0.0	0.0

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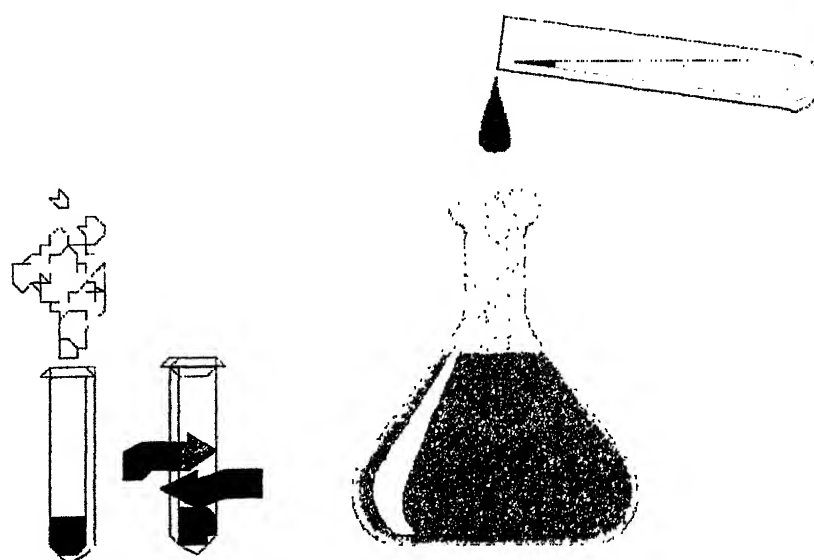
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CHAPTER 6

ISEs of Mn (II), Fe (III), Cu (II),
Zn (II) and their
Applications in
*Manganite, Haematite,
Clay Iron Stone, Copper Pyrite,
Zinc Blende, Calamine and Soils*



ISEs OF SOME TRANSITION METALS AND THEIR APPLICATIONS

6.1 INTRODUCTORY

This chapter deals with the fabrication, characteristics as well as applications of some new transition metal ion selective electrodes. These new electrodes were for Mn (II), Fe (III) Cu (II) and Zn (II) ions were used for the analysis of following naturally occurring minerals, *manganite, haematite, clay iron stone, copper pyrite, zinc blende, calamine* and *soils*. Before presenting work, a literature survey on these electrodes have been summarised in Table 6.1.

Table: 6.1

ISE Sensitive to Manganese (II), Iron (III), Copper (II) and Zinc (II)

ISE	Electroactive Material	Matrix	References
Mn (II)	Manganese chalcogenide + Ag ₂ S (Homogeneous)	—	1
	Mn ₃ (PO ₄) ₂ (Heterogeneous)	Silicon rubber	2
	MnHPO ₄	—	3
	Mn(II) telluride +Silver sulphide	—	4
	Mn(II) based on ion exchange resin	Epoxy resin	5
	Mn (IV) Oxide	—	6
	Mn(II) + 8- hydroxy quinoline	Epoxy resin	7
	Tetrapyridine Mn (II) thiocyanate (CWISE)	PVC	8
	Mn (II)- pyrophosphate	Silicon rubber	9

ISE	Electroactive Material	Matrix	References
	Pyrite + α - bromonaphthalene	—	10
	Manganese diethyldithiocarbamate	Epoxy resin	This work
Fe (III)	Iron (III) + tin (IV) arsenate (Heterogeneous)	Epoxy resin	11
	Iron (II) + phthalocyanine	—	12
	Iron (III) + quinol	Epoxy resin	This work
Cu (II)	Clay membrane	—	13,14
	Moulded cation exchanger	—	15
	Cation exchange resin	—	16
	CuI	Vinyl chloride	17
	CuS	MeCN	18
	Cu ₂ S	Silicon rubber	19
	Copper Selenide	—	20
	Cu Te- Ag ₂ S	—	21
	Cu (Py) ₂ (SCN) ₂	—	22
	Cu(II)- Pyrrolidine dithiocarbamate	—	23,24
	Bis (Ethylenediamine)Cu(II) tetra iodomercurate	Epoxy resin	25
	Cu (CH ₃ CN) ₄ ClO ₄	—	26
	CuAgSe and Cu _{2-x} — Se	—	27
	Copper tungstoarsenate	—	28
	Cu (II) Xylene Bis (diethyl dithio carbamate)	PVC	29
	Cu(II) thiuram disulphide	—	30
	Cu (II) diethyldithio- phosphate	CCl ₄	31

ISE	Electroactive Material	Matrix	References
	Cu -TTBA [1-(2',3',5',. tri-o- benzoyl-β-D-ribofuranosyl)-4- thioxo-5- benzylthio-6- azauracil]	CHCl ₃	32
	Cu (II)- Chalcogenide glass	Resin	33
	Copper- rubeanate	Epoxy resin	This work
	Copper diethyldithiocarbamate	Epoxy resin	This work
Zn(II)	ZnS + Ag ₂ S	—	34
	Zn- Chalcogenide +Ag ₂ S	—	35
	ZnSe/Ag ₂ S	—	36
	Tetracyanozincate	Silicon rubber	37
	Quaternary NH ₄ ⁺ salt (ZnCl ₄) ²⁻	—	38
	Zn(II)- di-n-octylphenyl phosphate	—	39
	Zn(99.99.wt%)	—	40
	Zinc dithiozonate	—	41
	Zn (SCN) ₄ ²⁻	—	42
	Zn Te or Zn ₂ Te-Ag ₂ S	—	43
	Zinc complex of uric acid	Epoxy resin	This work
	Zinc diethyldithiocarbamate	Epoxy resin	This work.

6.2 MANGANESE AND IRON ION SELECTIVE ELECTRODES

For fabrication of Mn (II) and Fe (III) ISEs two different electroactive materials, *manganese diethyldithiocarbamate* and *iron quinol* were used. The method of preparation of these electroactive materials is described in chapter 3. Both the electroactive materials mixed separately with epoxy resin in 1:4 ratio to form a master membrane as described in chapter 2. A small piece of this membrane was cut and plugged at the one end of the barrel shaped tube. 0.1 mol dm⁻³ solution of Mn (II) ion in case of Mn (II) ISE, and 0.1 mol dm⁻³ solution of Fe (III) ion in case of Fe (III) ISE was filled inside the tube. A saturated calomel electrode was inserted inside the tube for electrical contact and a secondary calomel electrode was used as external reference electrode. The electrode assembly can be represented as:

For Mn (II) ISE

SCE	0.1mol dm ⁻³ MnCl ₂ solution	Membrane	Sample solution	SCE
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For Fe (III) ISE

SCE	0.1mol dm ⁻³ FeCl ₃ solution	Membrane	Sample solution	SCE
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6.2.1 Characteristics Of Electrodes

Before making measurements the electrode assembly was dipped into 0.01 mol dm⁻³ solution of Mn (II) or Fe (III) ion as the case may be for 10 days. After conditioning the electrodes, various parameters were studied. A Philips pH meter (PR 9405) was used for potential measurements. All the measurements were carried out at room temperature (25±2°).

6.2.1.1 Electrode Response

A set of solutions of various concentrations from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ of MnCl_2 and FeCl_3 were prepared for both the electrodes. In case of FeCl_3 solution the pH was maintained below 3 by adding dil hydrochloric acid for avoiding hydrolysis. The electrode potentials were noted in each case (Table 6.2). The concentrations of the ion were plotted against the electrode potentials on a semi log graph paper. A linear response was observed for Mn(II) ISE down to $5 \times 10^{-5} \text{ mol dm}^{-3}$ with a slope 38 mV per decade change in Mn(II) ion concentration (Fig. 6.1).

In case of Fe (III) ISE, a linear response was observed down to $1 \times 10^{-4} \text{ mol dm}^{-3}$ with a slope 35 mV per decade change in Fe (III) ion concentration (Fig. 6.2).

6.2.1.2 Response Time

To find out the response time for both the electrodes, the electrode was first dipped in 0.1 mol dm^{-3} solution of MnCl_2 or FeCl_3 . The concentration of the solution was suddenly changed to 0.01 mol dm^{-3} . The value of potential change was noted every 5 seconds (Table 6.3). A constant potential was obtained after 30 seconds for Mn(II) ISE and 25 seconds for Fe(III) ISE (Fig. 6.3).

6.2.1.3 Effect Of pH

To study the effect of pH, a series of solutions of varying pH were prepared by keeping the concentration of metal ion constant at 0.01 mol dm^{-3} . The potential of each solution was recorded (Table 6.4) for both the electrodes and it was found that the potential remained unchanged within the pH range 2 to 7 for Mn(II) ISE and 1 to 3 for Fe (III) ISE (Fig.6.4). In case Fe (III) ISE it was observed that near pH 3 the hydrolysis occurs.

Table: 6.2
Electrode Response

Concentration of metal ion (mol dm ⁻³)	Electrode Potential (mV)	
	Mn(II) ISE	Fe(III) ISE
1x10 ⁻¹	214	272
5x10 ⁻²	200	265
1x10 ⁻²	175	242
5x10 ⁻³	160	228
1x10 ⁻³	134	200
5x10 ⁻⁴	120	185
1x10 ⁻⁴	94	162
5x10 ⁻⁵	90	162
1x10 ⁻⁵	90	162
5x10 ⁻⁶	90	162
1x10 ⁻⁶	90	162

Table: 6.3
Response Time

Time (sec)	Electrode Potential (mV)	
	Mn(II) ISE	Fe(III) ISE
0	215	275
5	200	270
10	190	260
15	185	250
20	180	245
25	170	240
30	170	240
35	170	240
40	170	240
45	170	240
50	170	240

FIG. 6.1 : Potential vs -log Concentration of Mn(II) Ion
in Presence and Absence of Secondary Ions

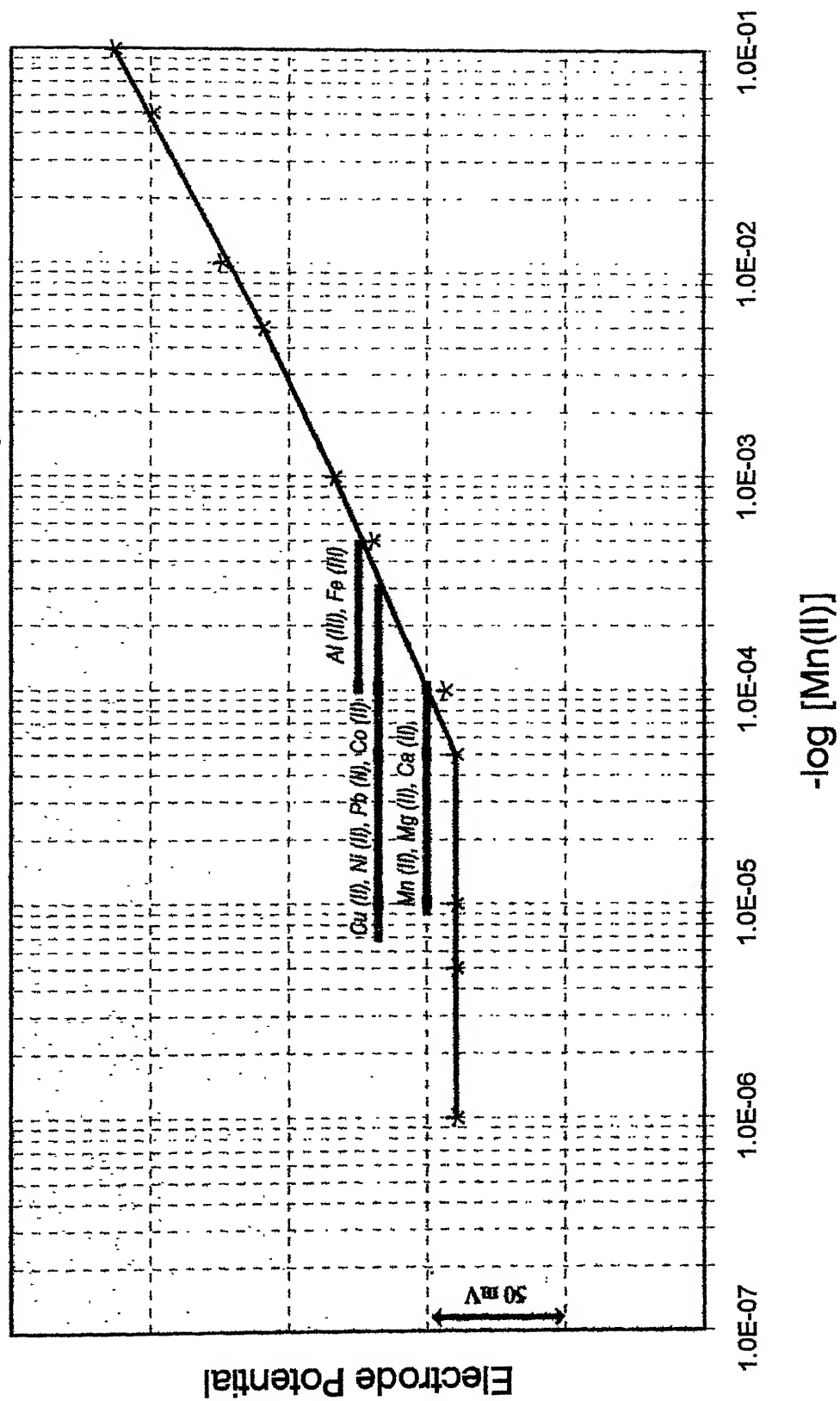


FIG. 6.2 : Potential vs -log Concentration of Fe(III) Ion
in Presence and Absence of Secondary Ions

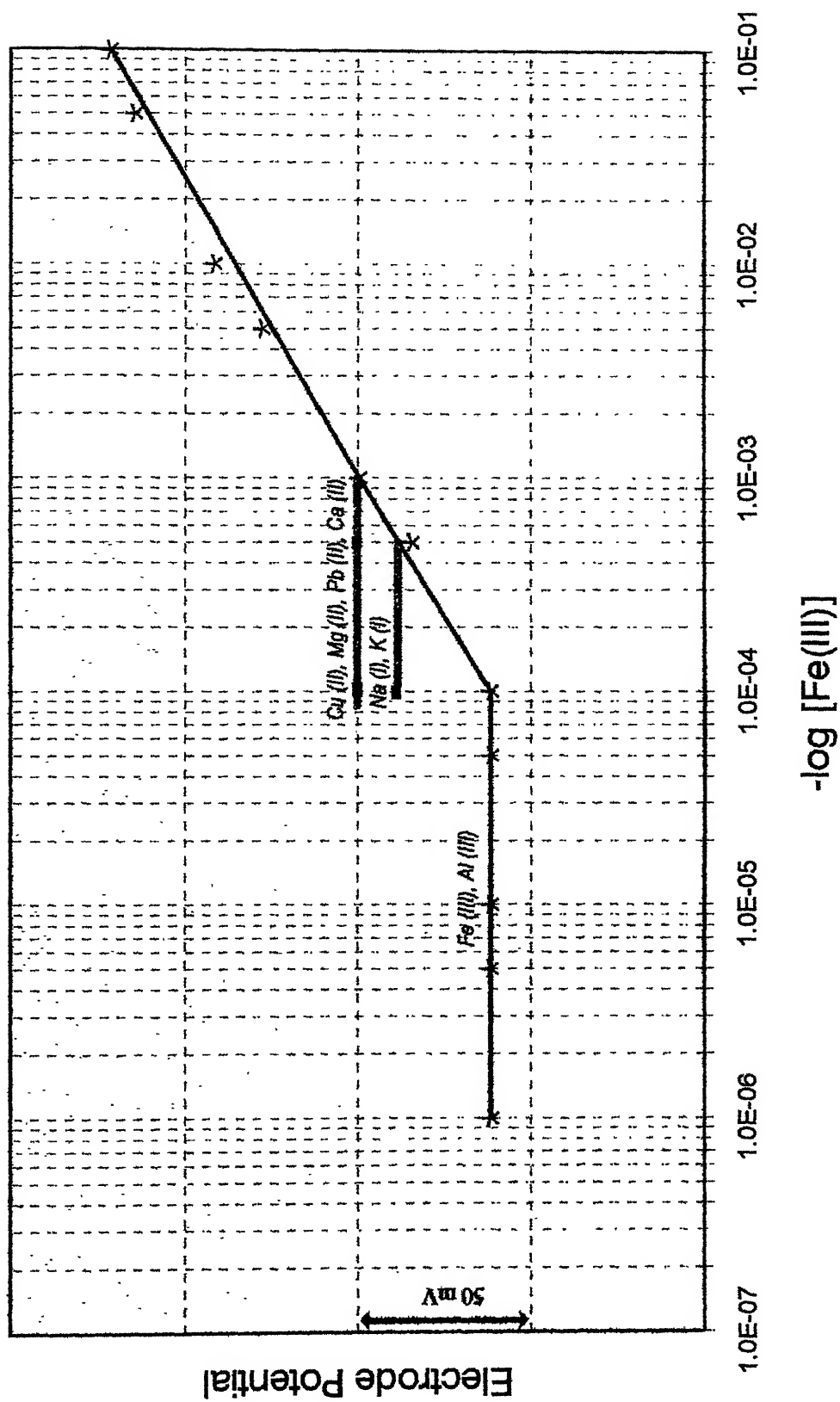


Table: 6.4
Effect of pH

pH	Electrode Potential (mV)	
	Mn(II) ISE	Fe(III) ISE
1	115	68
2	125	68
3	125	68
4	128	85
5	125	110
6	125	—
7	126	—
8	145	—
9	150	—
10	—	—

6.2.1.4 Selectivity Coefficients

The selectivity coefficients for different cations were determined by mixed solution method for both the electrodes. A set of solutions were prepared in which the concentration of interfering ion was kept constant ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and concentration of primary ion varied from $1 \times 10^{-1} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$. The selectivity coefficients for both the electrodes were calculated from the graph (Fig. 6.1 and 6.2) are given in Table 6.5.

FIG. 6.3 : Potential vs Time

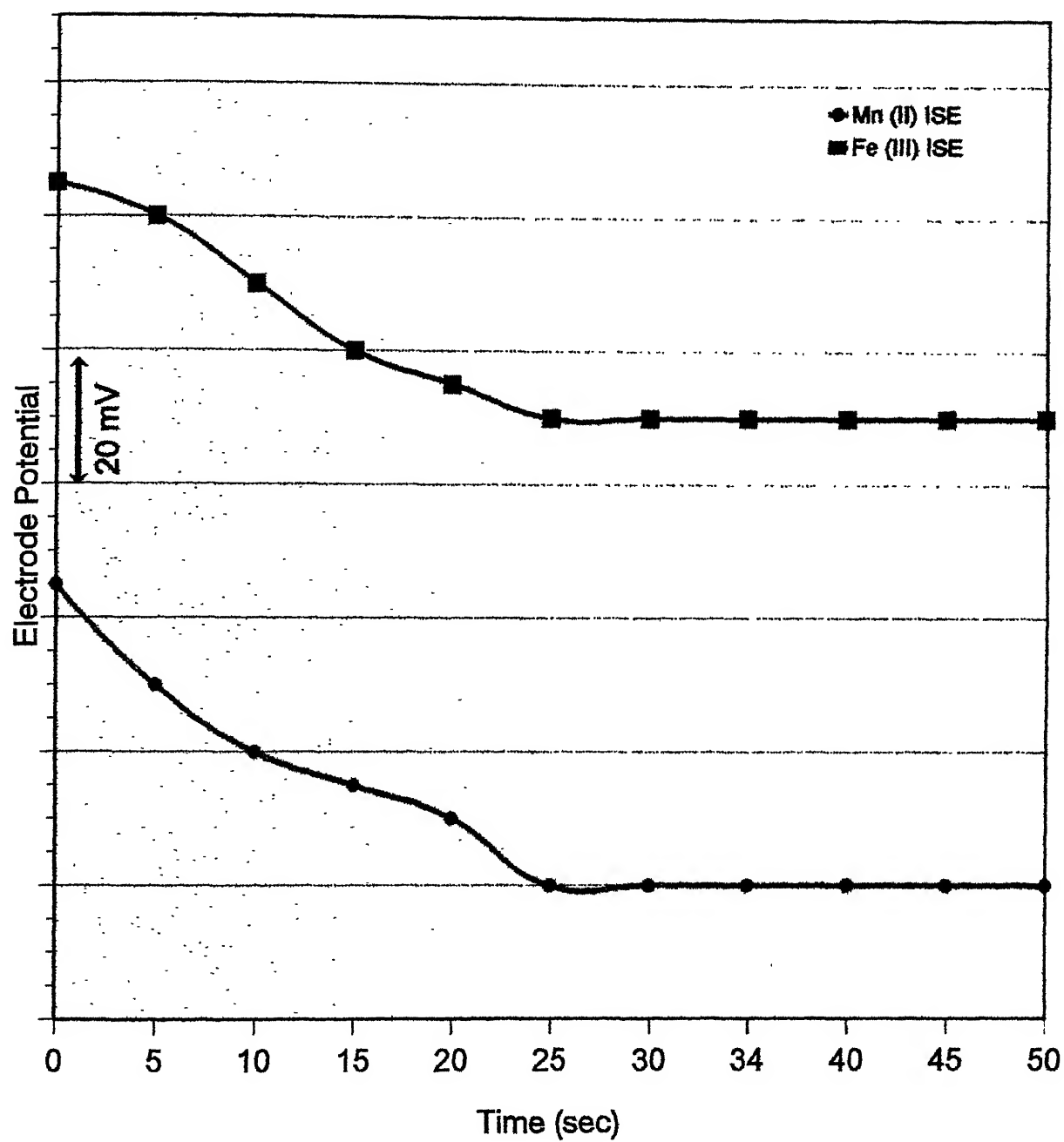


FIG. 6.4 : Potential vs pH

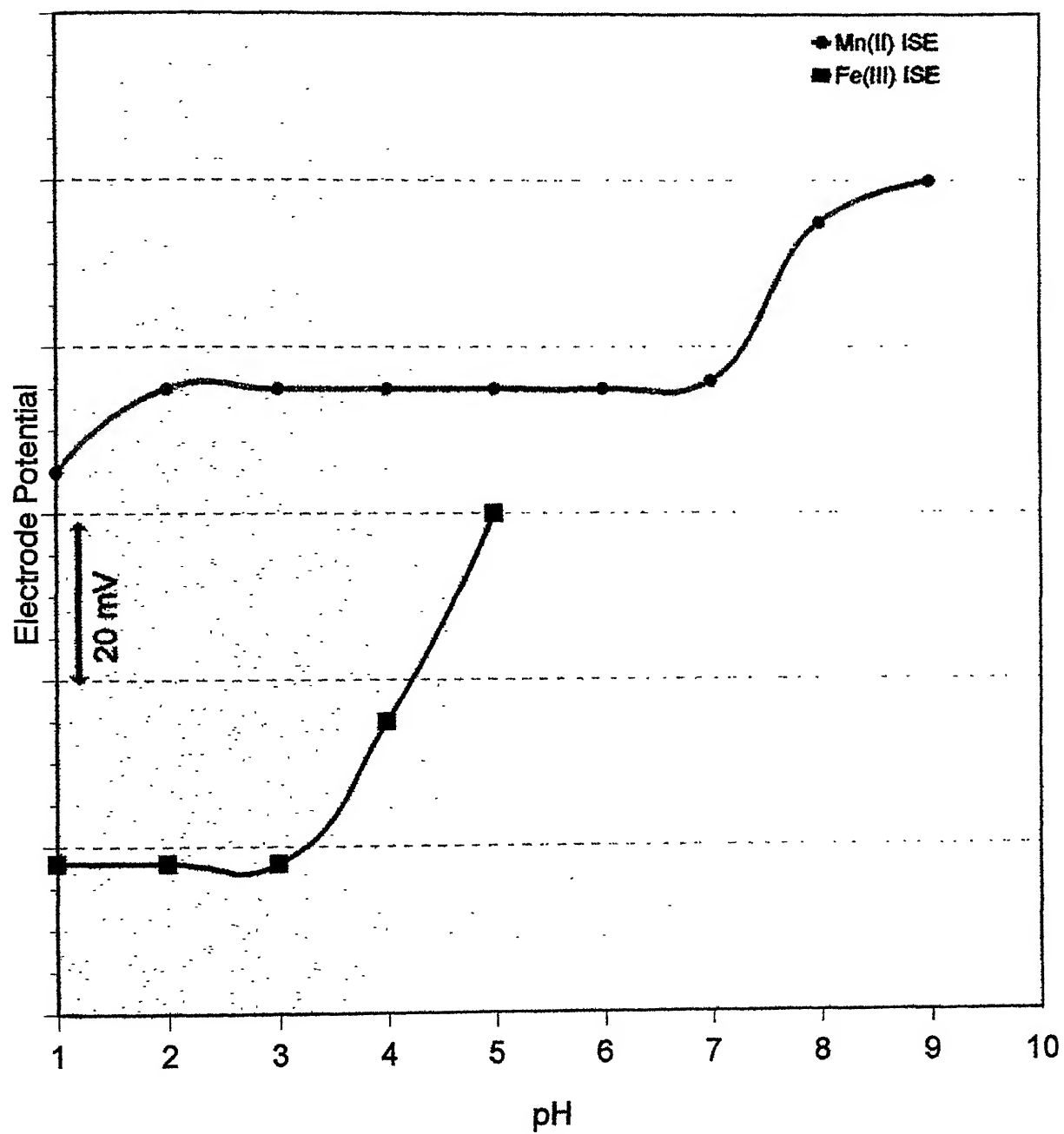


Table: 6.5
Selectivity Coefficients

Ions	$K_{Mn^{2+},M}^{pot}$	Ions	$K_{Fe^{3+},M}^{pot}$
Ni(II)	0.300	Pb(II)	0.01
Co(II)	0.300	Cu(II)	0.01
Cu(II)	0.300	Na(II)	0.50
Pb(II)	0.300	K(I)	0.10
Fe(II)	0.100	Al (III)	0.10
Fe(III)	0.005	Ca(II)	0.01
Al(III)	0.005	Mg(II)	0.01
Ca(II)	0.100	—	—
Mg(II)	0.1	—	—

6.2.1.5 Life Time

It was observed that Mn (II) ISE give stable potential up to 6 months and the Fe (III) ISE give stable potential up to 4 months. After this time both the electrodes show erratic behaviour. Therefore, the life time of Mn (II) ISE is 6 months and Fe (III) ISE is 4 months.

6.2.2 Applications

To see the utility of the electrodes, prepared Mn(II) electrode was used as an indicator electrode in the precipitation titration. Both the electrodes were also used in the direct determination of Mn(II) and Fe (III) ion in naturally occurring minerals and soil samples.

6.2.2.1 Titration of Manganese Chloride against Diammonium Hydrogen phosphate

The prepared Mn(II) electrode was used as an indicator electrode in the precipitation titration of $MnCl_2$ solution against diammonium hydrogen phosphate $((NH_4)_2HPO_4)$. For this 10 ml of 0.01 mol dm^{-3} $MnCl_2$ solution

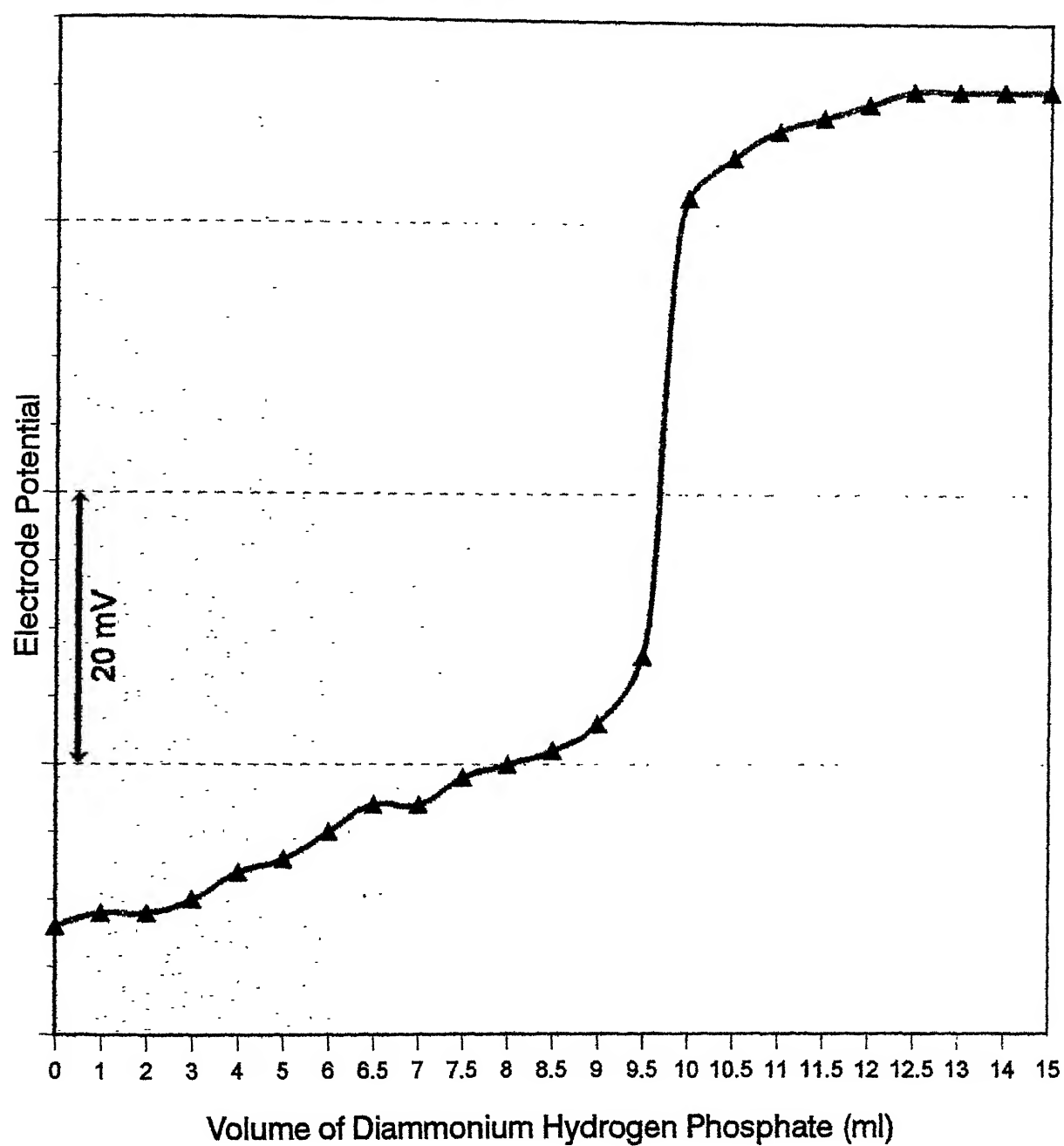
was pipetted out in a beaker and titrated against $0.01 \text{ mol dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ solution. The potential was noted (Table 6.6) after each addition of 0.5 ml of titrant from microburette. Potentials were plotted against the volume of diammonium hydrogen phosphate used (Fig. 6.5). It was observed that a sharp rise in the titration curve at the equivalence point.

Table: 6.6

Titration of Manganese Chloride against Diammonium Hydrogen phosphate

Volume of Titrant (ml)	Electrode Potential (mV)
0.0	58
1.0	59
2.0	59
3.0	60
4.0	62
5.0	63
6.0	65
6.5	67
7.0	67
7.5	69
8.0	70
8.5	71
9.0	73
9.5	78
10.0	112
10.5	115
11.0	117
11.5	118
12.0	119
12.5	120
13.0	120
14.0	120
15.0	120

FIG. 6.5 : Titration of Manganese Chloride vs
Diammonium Hydrogen Phosphate



6.2.2.2 Determination of Manganese In Manganite

1.0g of manganite was taken in a beaker. The sample was dissolved by heating the sample with a amount of 1ml of concentrated hydrochloric, 1ml of concentrated nitric, 1ml of hydrofluoric and 1ml of perchloric acids (44). The solution was evaporated to copious fumes and cooled. After cooling, 10ml of distilled water was added and again evaporated to copious fumes. The solution was cooled and pH was adjusted to 6.5 by adding dil NaOH. The solution was made up to 100ml and potential was recorded (Table 6.8). The amount of Mn(II) was calculated from the calibration curve (Fig. 6.6).

The manganese content in manganite was also studied at the Research and Development Laboratory, IFFCO, Phulpur by AAS technique. The AAS instrument was set at 279.5 nm wavelength (λ_{\max}) and slit 0.2nm. The air-acetylene flame was used. The amount of Mn(II) was then determined (Table 6.8). It was found that there is a fairly good agreement between the values obtained by both the methods.

6.1.3.3 Determination of Iron In Haematite and Clay Iron Stone

0.2g of haematite and 1.0g of clay ironstone (described in chapter 2) was taken in separate beakers. The sample was treated with 15 ml of concentrated hydrochloric acid. The solution was heated on a hot plate for some time and then kept near the boiling point of the acid until the undissolved residue, if any becomes perfectly white.

The residue was dissolved in distilled water, filtered into flask and made up to 100ml by adding distilled water. The potential was recorded (Table 6.7) and converted into metal ion concentration and the content of Fe (III) was calculated from calibration curve (Fig. 6.7).

The amount of Fe (III) was also determined by AAS technique at Research and Development Laboratory, IFFCO, Phulpur. For this the instrument was set at wavelength (λ_{\max}) 248.3nm, slit 0.2nm and flame

air- acetylene was used. The value of Fe (III) then recorded (Table 6.7) for both the samples and it was found that there is good agreement between the values obtained by both the methods.

6.2.2.4 Determination Of Manganese and Iron In Soils

Six soils were studied for determination of manganese and iron content. 1.0g of soils S₁, S₂, S₃, S₄, S₅ or S₆ as described in chapter 2 were taken in different beakers and soil extract was prepared by using the method describe in chapter 2. In case of iron determination the pH was adjusted at 1 by adding dil hydrochloric acid but in case of manganese determination there was no need for adjustment of pH. The solution was then made up to 100ml by distilled water and potential was recorded (Table 6.8). The amount of both the metals was calculated from the calibration curve for all the soil samples (Table 6.8, Fig. 6.6 and 6.8).

The AAS technique was also used for Mn(II) and Fe(III) content determination at Research and Development Laboratory, IFFCO, Phulpur. The instrument AAS was set at:

Metals	Wavelength (λ_{\max}) (nm)	Slit (nm)	Flame
Fe	248.3	0.2	air-acetylene
Mn	279.5	0.2	air-acetylene

The amount of manganese and iron content was present in soils then recorded (Table 6.8) and it was found that there is a good agreement for both the methods used.

Table: 6.7

Analysis of Manganite, Haematite and Clay Iron Stone

Sample	Electrode Potential (mV)	Amount of Fe(III) or Mn (II) by ISE (ppm)	Amount of Fe(III) or Mn (II) by AAS (ppm)
Manganite	151	142	140
Haematite	157	12565	12480
Clay Iron Stone	152	1452	1440

FIG. 6.6 : Determination of Mn(II) Ion in Manganite and Soils

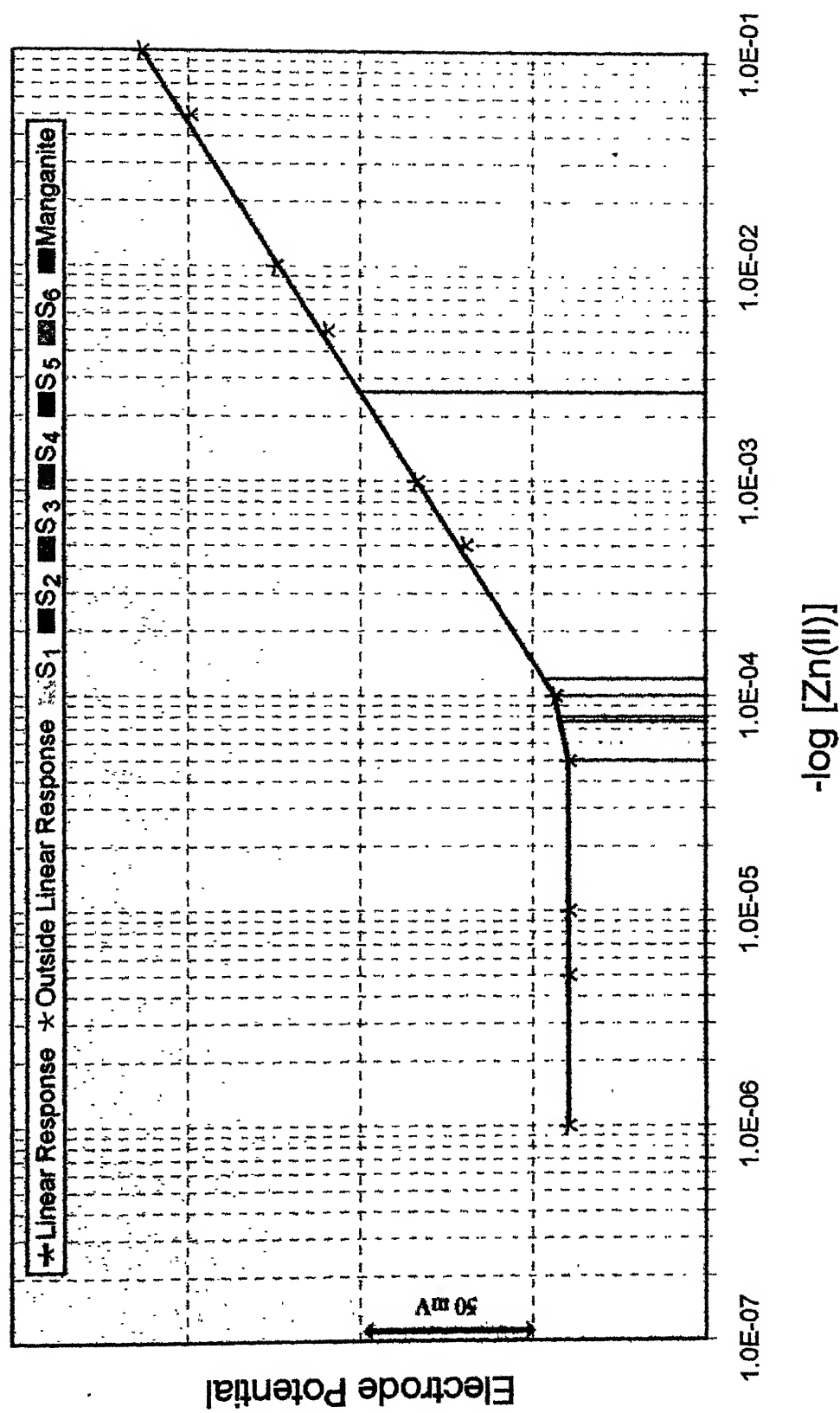


FIG. 6.7 : Determination of Fe(III) Ion in Clay Iron Stone and Haematite

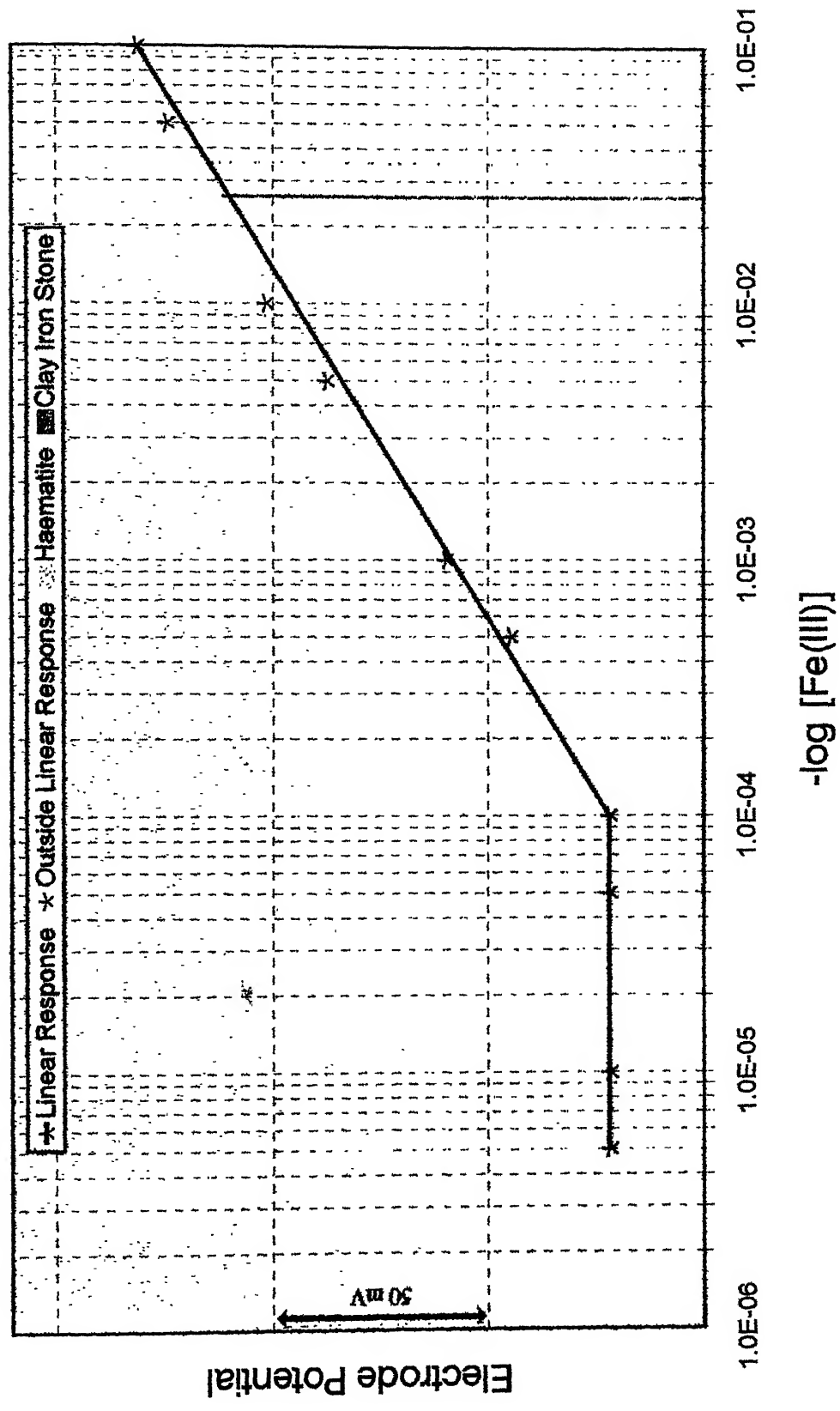


Table: 6.8
Analysis of Soils

Soil Samples	Mn(II) Content			Fe (III) Content		
	Electrode Potential (mV)	Amount of Mn(II) by ISE (ppm)	Amount of Mn(II) by AAS (ppm)	Electrode Potential (mV)	Amount of Fe(III) by ISE (ppm)	Amount of Fe(III) by AAS (ppm)
S ₁	90	3.2	3.4	194	42	42
S ₂	92	4.3	4.3	195	44.6	44
S ₃	91	4.1	4.2	203	72	70
S ₄	90	2.7	2.6	193	52	52
S ₅	97	6.5	6.1	202	92	92
S ₆	94	5.4	5.5	206	84	86

6.3 COPPER AND ZINC ION SELECTIVE ELECTRODES

Two different electroactive materials for both the electrodes were used. The method of preparation of these electroactive materials was described in chapter 3. For preparation of Cu(II) ISEs, *copper rubeanate*, *copper dethyldithiocarbamate* and for Zn(II) ISEs, *zinc urate*, *zinc diethyldithiocarbamate*, new electroactive materials were mixed separately in 1:4 ratio to form a master membrane of 0.5 mm in thickness as described in chapter 2. The *copper rubeanate* was designated as *electrode-I* and *copper diethyldithiocarbamate* as *electrode II* in case of copper and in case of Zn (II) ISEs *zinc urate* was designated as *electrode I* and *zinc diethyldithiocarbamate* as *electrode II*. A small piece of this membrane was cut and plugged one end of barrel shaped tube. A saturated calomel electrode was inserted inside the tube. Which was filled with a solution of 0.1 mol dm⁻³ CuSO₄ ion in case of Cu (II) ISEs, while in case of Zn (II) ISEs 0.01 mol dm⁻³ solution of ZnCl₂ was filled inside the tube. A secondary calomel electrode was used as an external

reference electrode for electric current. The overall assembly can be represented as:

For Cu (II) ISEs

SCE	0.1mol dm ⁻³ CuSO ₄ solution	Membrane	Sample solution	SCE
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For Zn (II) ISEs

SCE	0.1mol dm ⁻³ ZnCl ₂ solution	Membrane	Sample solution	SCE
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6.3.1 Characteristics Of Electrodes

For conditioning the electrode, the assembly was dipped in 0.01 mol dm⁻³ solution- of Cu(II) and Zn (II) ions as the case may be, for one week. A Philips pH-meter (PR 9405) was used for measuring the potentials. All the measurements were carried out at room temperature (25±2°). The following parameters of both the electrodes were studied.

6.3.1.1 Electrode Response

After conditioning the electrodes, the electrode potentials for a series of standard solutions of CuSO₄ and ZnCl₂ were measured (Table 6.9) by using all the electrodes prepared above. A linear response was observed for Cu(II) concentration down to 1x10⁻⁵ mol dm⁻³ with a slope 33 mV per decade change in Cu(II) ion concentration for *electrode I* (Fig. 6.9) and down to 5x10⁻⁵ mol dm⁻³ with a slope 37 mV per decade change in Cu (II) ion concentration for *electrode II* (Fig. 6.10).

In case of Zn (II) ISEs the linear response was observed down to 5x10⁻⁵ mol dm⁻³ with a slop 34 mV per decade change in Zn (II) ion concentration for *electrode I* and (Fig. 6.11) down to 1x10⁻⁵ mol dm⁻³ with a slope 32 mV per decade change in Zn (II) ion concentration for *electrode II* (Fig. 6.12).

Table: 6.9
Electrode Response

Concentration of metal ion (mol dm ⁻³)	Electrode Potential (mV)			
	Cu(II) ISE <i>Electrode I</i>	Cu(II) ISE <i>Electrode II</i>	Zn(II) ISE <i>Electrode I</i>	Zn(II) ISE <i>Electrode II</i>
1x10 ⁻¹	242	213	255	278
5x10 ⁻²	230	200	245	270
1x10 ⁻²	210	170	225	245
5x10 ⁻³	195	160	208	235
1x10 ⁻³	175	130	185	212
5x10 ⁻⁴	160	114	170	200
1x10 ⁻⁴	140	90	144	180
5x10 ⁻⁵	130	75	132	168
1x10 ⁻⁵	105	75	132	145
5x10 ⁻⁶	105	75	132	145
1x10 ⁻⁶	105	75	132	145

Table: 6.10
Response Time

Time (sec)	Electrode Potential (mV)			
	Cu(II) ISE <i>Electrode I</i>	Cu(II) ISE <i>Electrode II</i>	Zn(II) ISE <i>Electrode I</i>	Zn(II) ISE <i>Electrode II</i>
0	242	213	225	245
5	235	205	215	240
10	225	195	200	230
15	220	190	192	220
20	215	180	183	215
25	210	170	183	213
30	210	170	183	210
35	210	170	183	210
40	210	170	183	210
45	210	170	183	210
50	210	170	183	210

FIG. 6.9 : Potential vs -log Concentration of Cu(II) Ion
in Presence and Absence of Secondary Ions

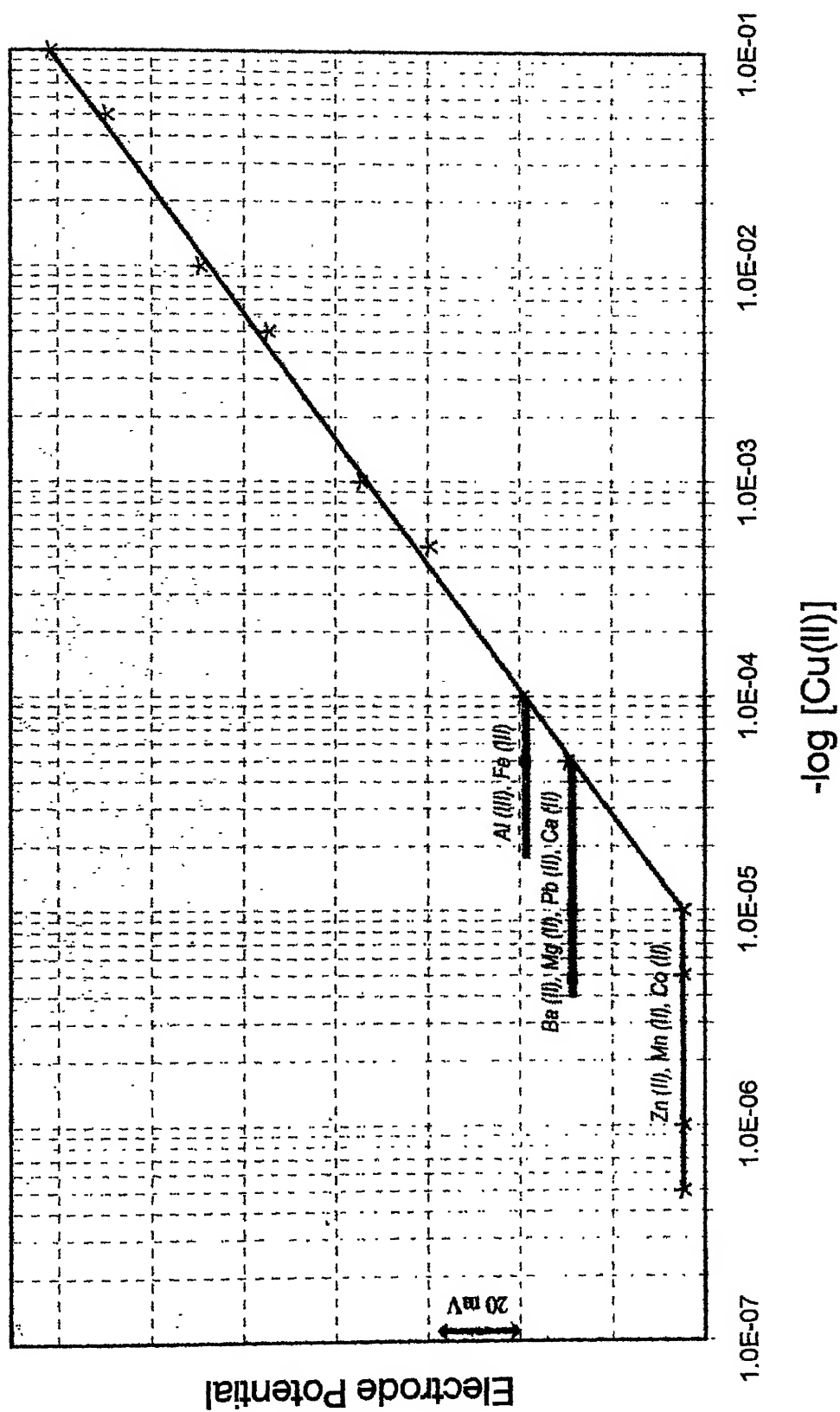


FIG. 6.10 : Potential Vs -log Concentration of Cu(II) Ion and Determination of Cu (II) Ion in Copper Pyrite

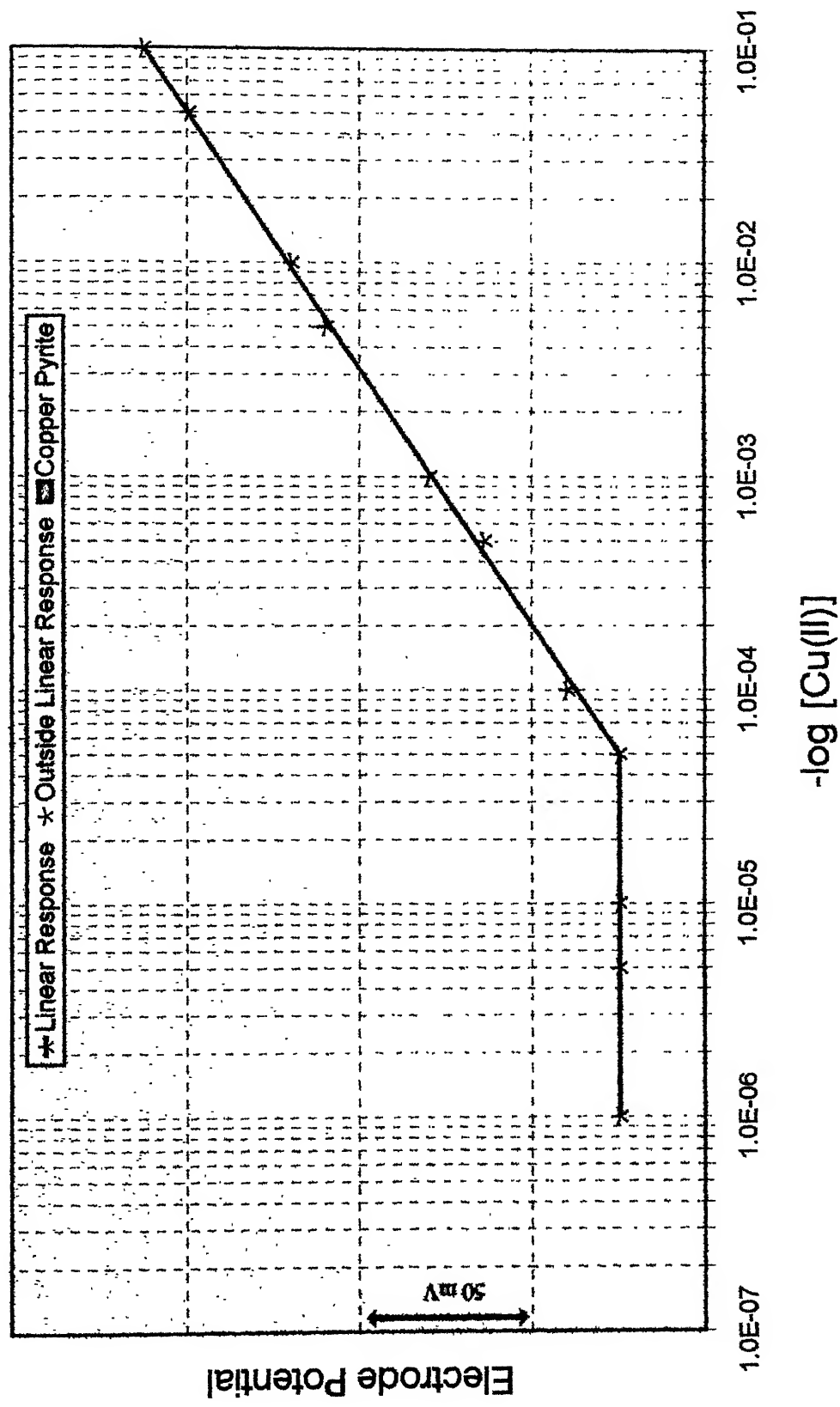


FIG. 6.11 : Potential vs -log Concentration of Zn(II) Ion
in Presence and Absence of Secondary Ions

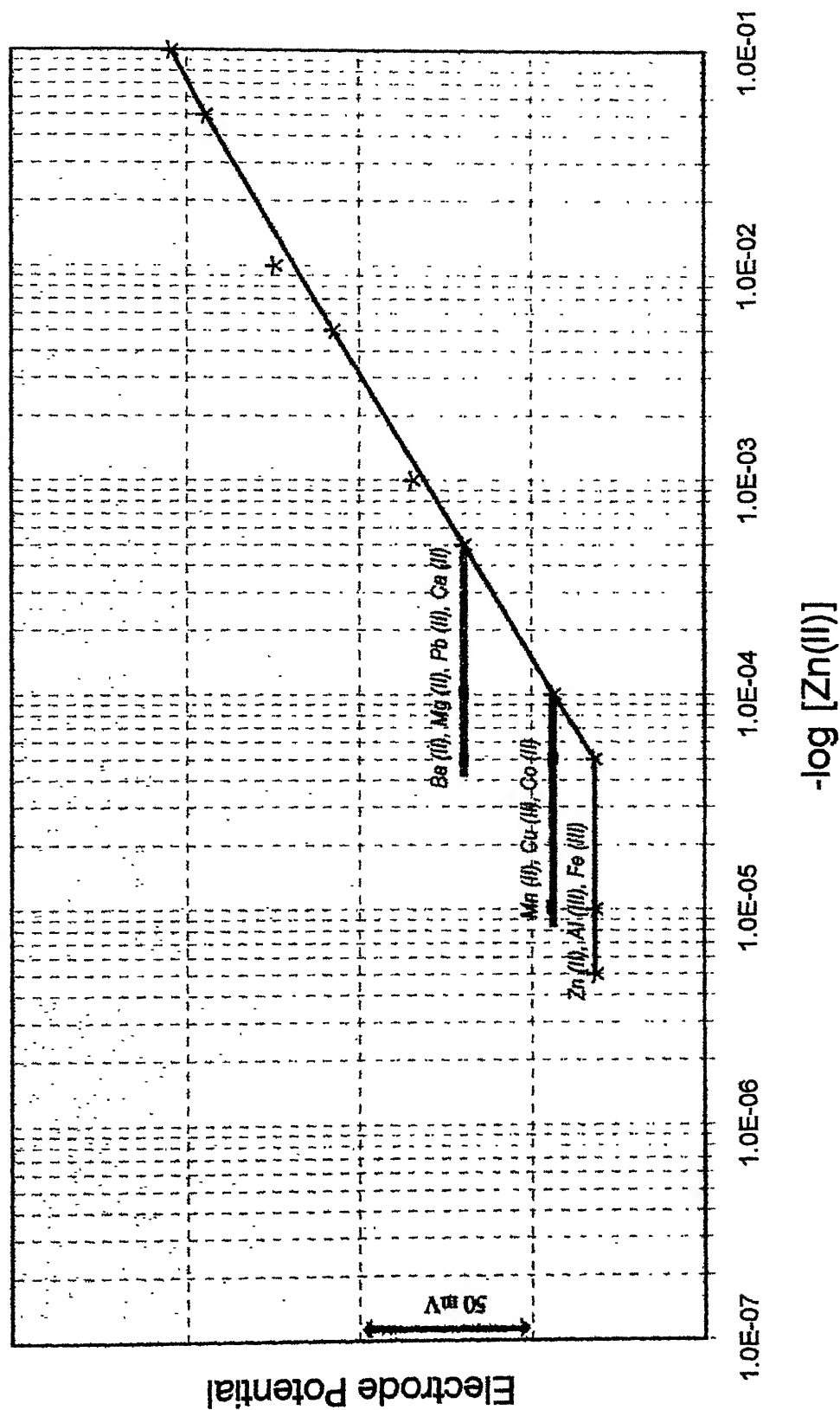


FIG. 6.12 : Potential vs -log Concentration of Zn(II) Ion and Determination of Zn(II) Ion in Soils

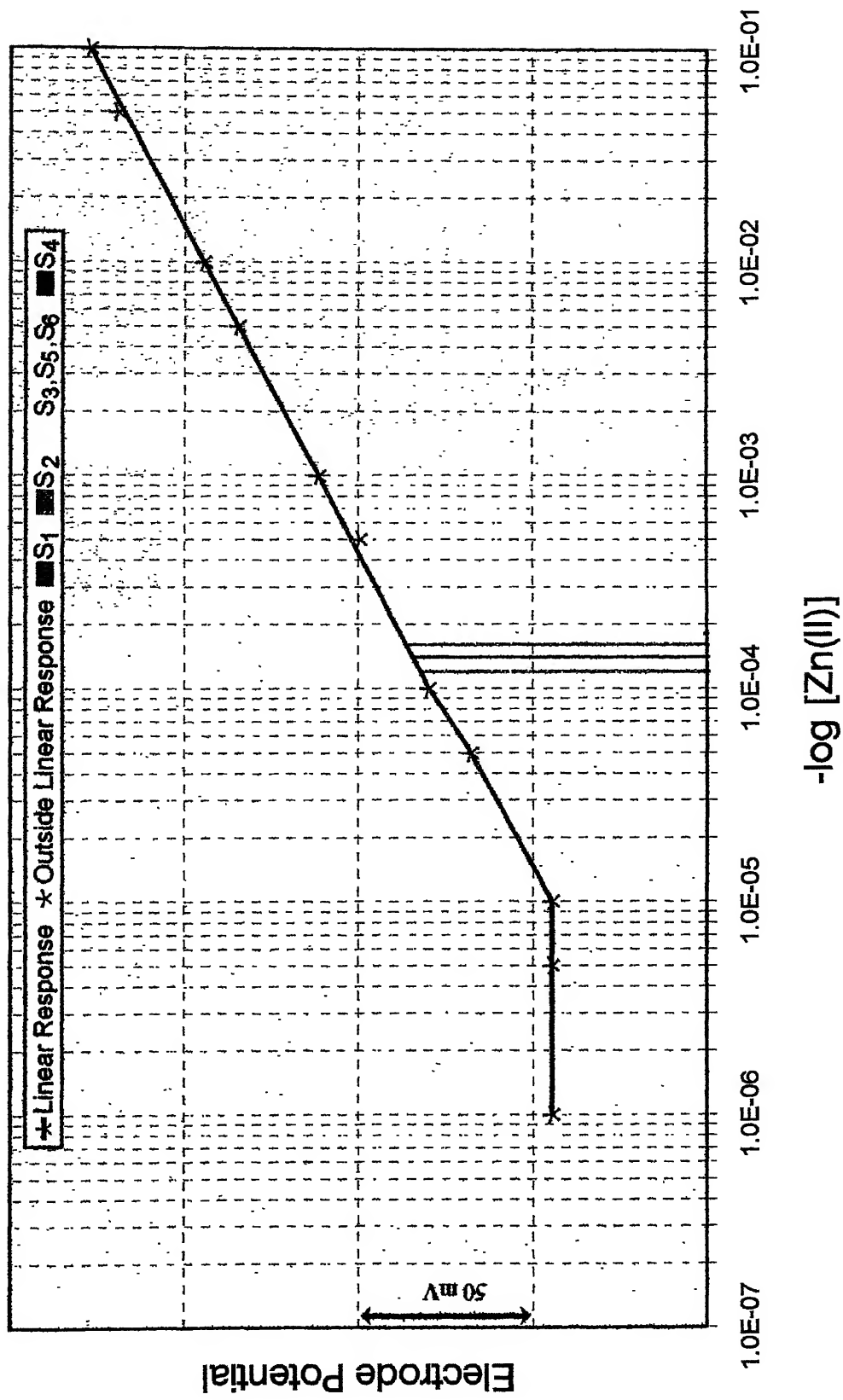


Table: 6.11
Effect of pH

pH	Electrode Potential (mV)			
	Cu(II) ISE <i>Electrode I</i>	Cu(II) ISE <i>Electrode II</i>	Zn(II) ISE <i>Electrode I</i>	Zn(II) ISE <i>Electrode II</i>
1	215	85	245	250
2	225	101	245	238
3	225	102	245	238
4	230	101	250	237
5	225	101	248	238
6	225	101	243	238
7	225	102	242	238
8	225	101	—	—
9	235	115	—	—
10	240	120	—	—

6.3.1.2 Response Time

In case of Cu(II) ISEs both the electrodes were dipped in 0.1 mol dm⁻³ CuSO₄ solution and suddenly the concentration of solution was change to 0.01 mol dm⁻³. The potentials for each electrode were recorded (Table 6.10) at every 5 seconds interval. It was clear from the graphs (Fig.6.13) that response time for both the Cu(II) ISE were 25.

In case of Zn(II) ISEs, both the electrodes were first dipped in 0.1 mol dm⁻³ solution of ZnCl₂ and the concentration was immediately changed to 0.01 mol dm⁻³. The potentials for each Zn(II) ISE's were recorded (Table 6.10) at every 5 seconds interval. These potentials were plotted against time (Fig. 6.14) and it was clear from the graph a

constant potential was obtained after 20 seconds for *electrode I* and after 30 seconds for *electrode II*.

6.3.1.3 Effect of pH

A set of solutions of different pH was prepared for both the metal Cu (II) and Zn (II) ISEs keeping the concentration of metal ion constant (0.01 mol dm^{-3}). The potential of each solution was noted (Table 6.11) using Cu (II) ISEs as well as Zn (II) ISEs. It was found from the graphs (Fig. 6.15 and 6.16) that the potential remain unchanged within the pH range 2 to 8 for both the Cu (II) ISE's and 1 to 7 for *electrode I* Zn (II) ISE and 2 to 7 for *electrode II* Zn (II) ISE.

6.3.1.4 Selectivity Coefficient

The selectivity coefficients for different cations for both the ISEs were determined by mixed solution method as described in chapter 2. The values of selectivity coefficients were calculated from graphs (Fig. 6.9 and 6.11) for Cu (II) ISE and Zn (II) ISE and are given in Table 6.12.

Table: 6.12

Selectivity Coefficients

Ions	$K_{\text{Cu}^{2+}, \text{M}}^{\text{pot}}$	$K_{\text{Zn}^{2+}, \text{M}}^{\text{pot}}$
Ba (II)	0.050	0.5000
Mg (II)	0.050	0.5000
Ca (II)	0.050	0.5000
Pb (II)	0.050	0.5000
Mn(II)	0.010	0.1000
Zn (II)	0.010	—
Co (II)	0.010	0.1000
Al (III)	0.001	0.0005
Fe (III)	0.001	0.0005
Cu (II)	—	0.1000

FIG. 6.13 : Potential vs Time

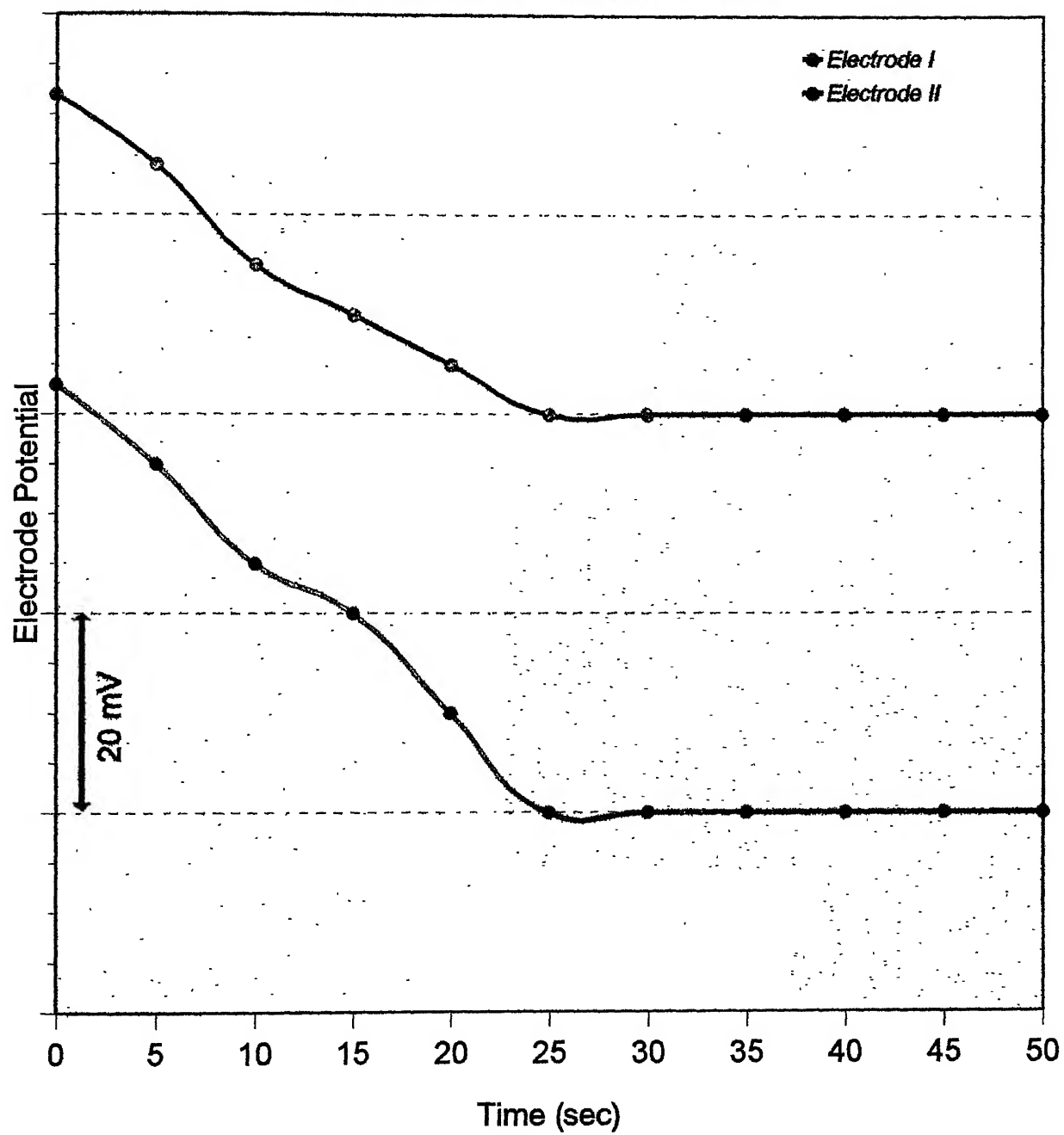


FIG. 6.14 : Potential vs Time

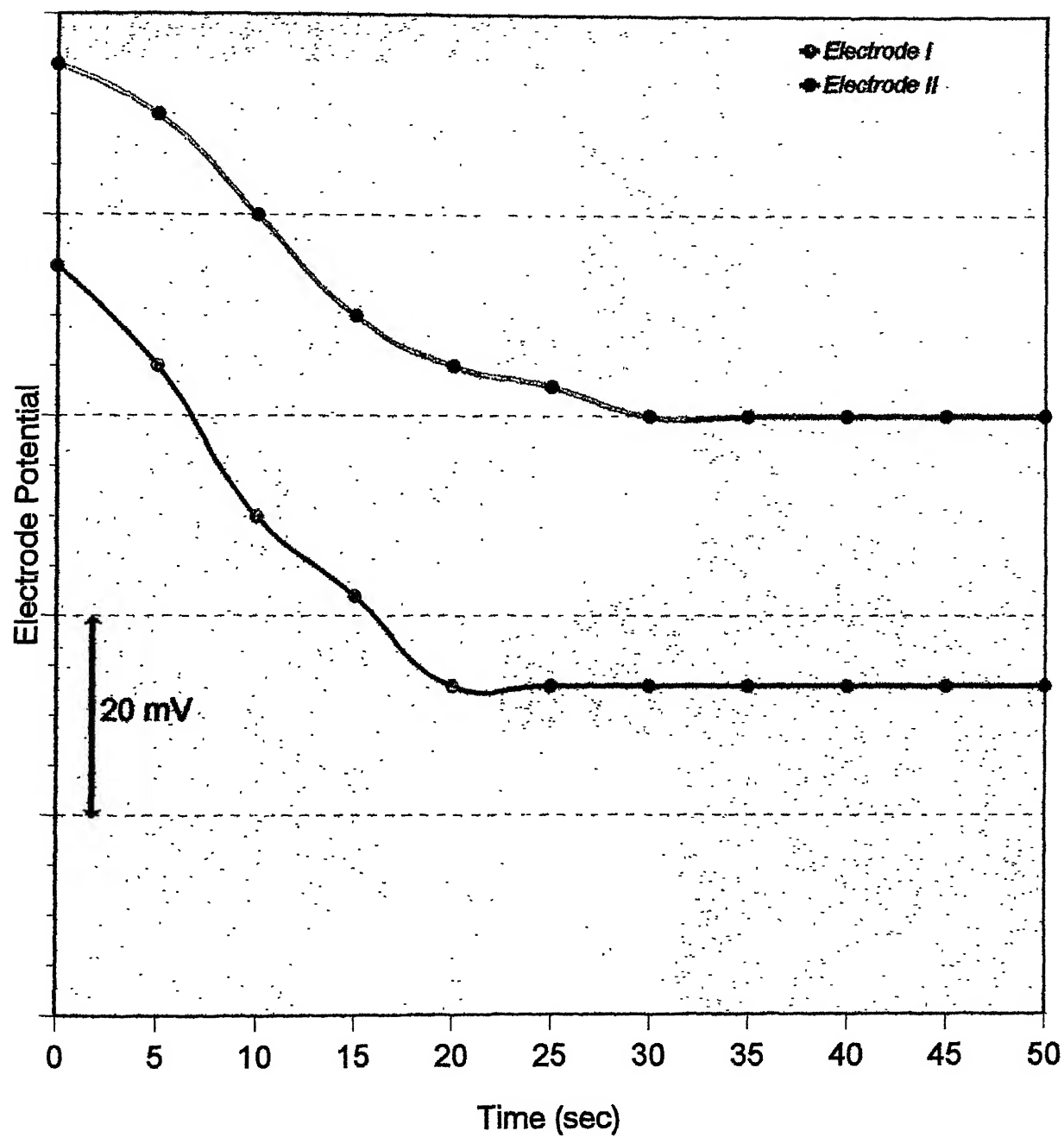


FIG. 6.15 : Potential vs pH

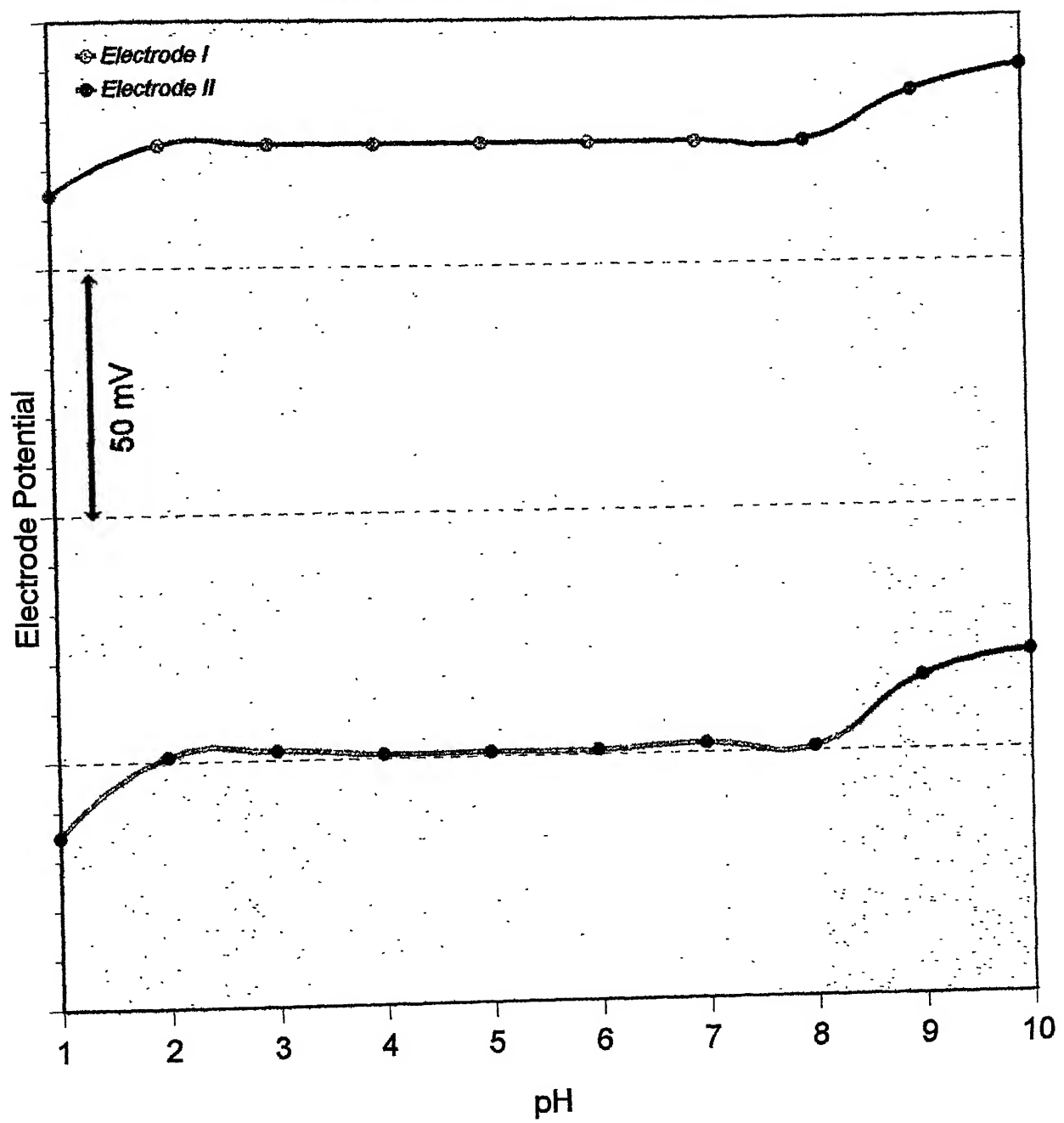
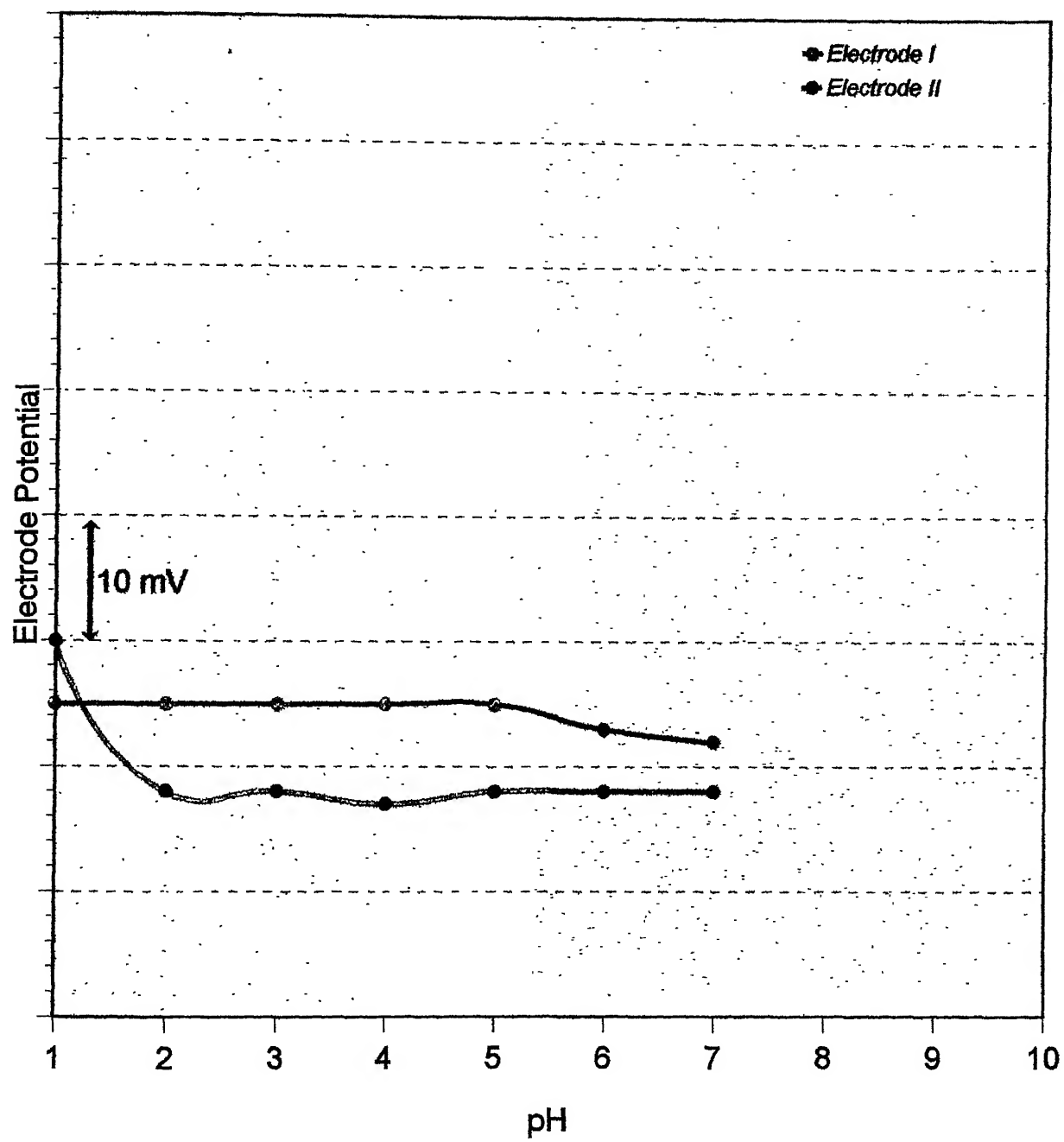


FIG. 6.16 : Potential vs pH



6.3.1.5 Life Time

After one week the electrode gave constant potential up to 8 months. After this time the electrodes give some erratic behaviour. Therefore, the lifetime of all the electrodes are approximately 8 months.

6.3.2 Applications

To see the utility of above prepared Cu (II) ISEs and Zn (II) ISEs, both the electrodes were used as an indicator electrode in the precipitation titration and also used in the direct determination of Cu (II) and Zn (II) content in following naturally occurring minerals *copper pyrite, zinc blende, calamine* and *soil samples*.

6.3.2.1 Titration of Copper Sulphate against EDTA

The Cu (II) ISEs prepared above was used as an indicator electrode in the precipitation titration of 0.01 mol dm^{-3} of CuSO_4 against 0.01 mol dm^{-3} of EDTA using buffer solution (acetic acid + sodium acetate) at pH 4.6. For this 10 ml of 0.01 mol dm^{-3} solution of CuSO_4 was taken in beaker and 5 ml buffer solution was added. This solution was titrated against 0.01 mol dm^{-3} of EDTA solution added from a microburette. The potential change was noted (Table 6.13) after each small addition of titrant. The values were then plotted against the volume of titrant consumed (Fig. 6.17). It was observed that a sharp rise in the titration curve near the end point.

6.3.2.2 Titration Of Zinc Chloride against Potassium Ferrocyanide

The Zn(II) ISEs prepared were also used as an indicator electrode in the precipitation titration of 0.01 mol dm^{-3} ZnCl_2 against 0.01 mol dm^{-3} of potassium ferrocyanide. For this 10 ml of 0.01 mol dm^{-3} ZnCl_2 solution was pipetted out in a beaker and titrated against 0.01 mol dm^{-3} of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. The potentials were noted (Table 6.14) after each small addition of titrant from a microburette. These values were then

plotted against the volume of titrant consumed (Fig. 6.18). It was observed that a sharp rise in the titration curve near the equivalence point.

Table: 6.13
Titration of Copper Sulphate against EDTA

Volume of Titrant (ml)	Electrode Potential (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0.0	45	50
1.0	46	51
2.0	48	53
3.0	49	55
4.0	50	57
5.0	52	69
6.0	54	61
7.0	56	63
7.5	57	65
8.0	58	67
8.5	60	70
9.0	62	74
9.5	70	80
10.0	105	115
10.5	109	117
11.0	111	119
11.5	112	120
12.0	113	120
13.0	115	121
14.0	115	121
15.0	115	121

FIG. 6.17 : Titration of Copper Sulphate
vs EDTA

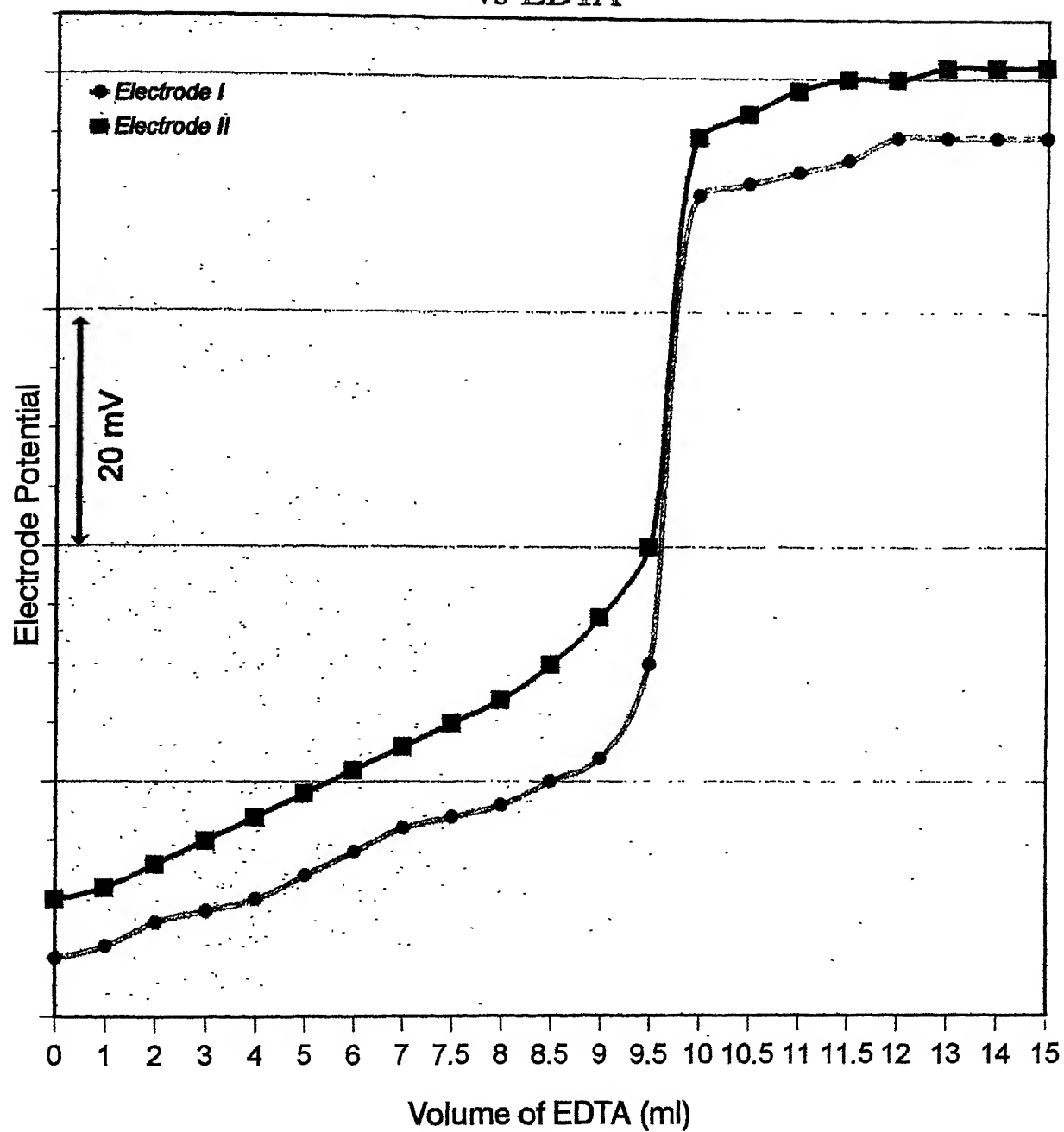


FIG. 6.18 : Titration of Zinc Chloride vs
Potassium Ferro Cyanide

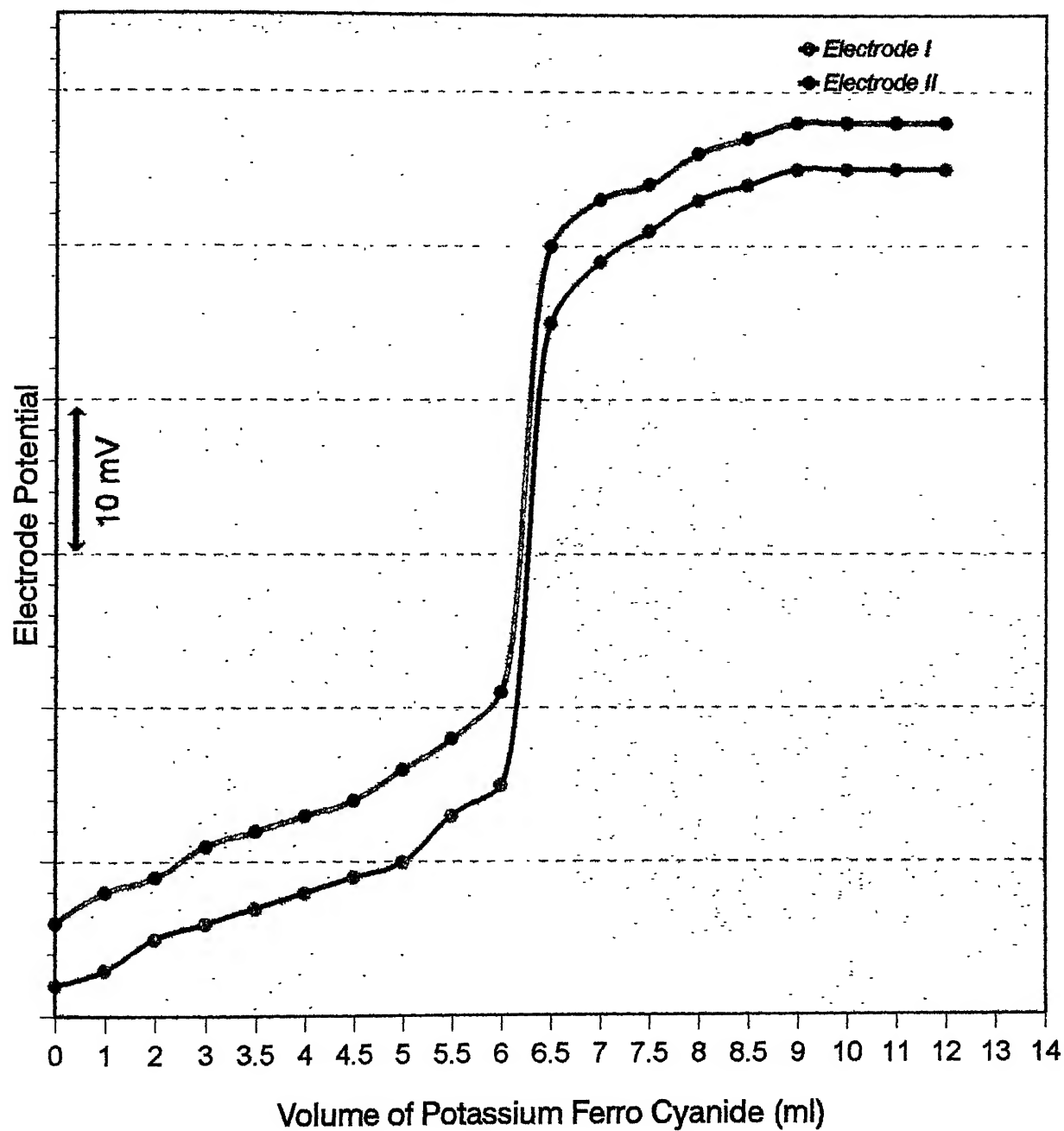


Table: 6.14**Titration Of Zinc Chloride against Potassium Ferrocyanide**

Volume of Titrant (ml)	Electrode Potentials (mV)	
	<i>Electrode I</i>	<i>Electrode II</i>
0.0	47	51
1.0	48	53
2.0	50	54
3.0	51	56
3.5	52	57
4.0	53	58
4.5	54	59
5.0	55	61
5.5	58	63
6.0	60	66
6.5	90	95
7.0	94	98
7.5	96	99
8.0	98	101
8.5	99	102
9.0	100	103
10.0	100	103
11.0	100	103
12.0	100	103

6.3.2.3 Determination Of Copper In Copper Pyrite

Copper pyrite is an important mineral of copper and mainly contains copper-iron sulphide. For determination of copper content in

pyrite, 1.0 g of sample was taken in a beaker and treated with 5ml of concentrated nitric and 5ml of concentrated sulphuric acids. The beaker was then heated on a hot plate so that there was a vigorous but not turbulent, evolution of brown fumes. There was no residue after about 15 minutes treatment. 20 ml of distilled water was added in the beaker and the pH was checked after cooling. It was found that the pH of the solution was within working range of electrode. The solution was made up to 100 ml by adding distilled water. The potential of the solution was noted using *electrode II* (Table 6.16) and converted into the metal ion concentration from calibration curve. The amount of copper content was calculated from the calibration curve (Fig. 1.10) and is given in Table 6.15.

The AAS technique was also used for the determination of copper content in pyrite. The study was carried out in the Research and Development Laboratory, IFFCO, Phulpur. For this the instrument was set at wavelength (λ_{max}) 324.8 nm, slit 0.7 nm and flame air-acetylene was used. The value then recorded (Table 6.15) and it was found that there was a good agreement between the values obtained by both the techniques.

6.3.2.4 Determination Of Zinc In Zinc Blende and Calamine

Both the minerals are naturally occurring of zinc metal. 1.0 g of zinc blende and calamine was taken in separate beakers and treated with 10 ml of concentrated hydrochloric and few drops of concentrated nitric acids. The beakers were heated on a hot plate until the residue became white. After cooling the beakers 10ml of distilled water was added in each sample to dissolve the residue. The pH was checked and it was found that in both the cases the pH was within the working range of electrode. Then the volume made up to 100 ml by adding distilled water. The potential was recorded using *electrode I* (Table 6.15) in each case and potential was converted to the concentration of Zn(II) ion and then the

amount of zinc content was calculated from the calibration curve (Fig. 6.19).

The AAS technique was also used for the determination of zinc content in both the minerals. The study was carried out at Research and Development Laboratory, IFFCO, Phulpur. The AAS was set at wavelength (λ_{max}) 213.9nm, slit 0.7nm and flame air acetylene was used. The amount of zinc content then recorded (Table 6.15) and it was observed that there is fairly good agreement between the values obtained from both the methods.

Table: 6.15

Analysis of Copper pyrite, Zinc blende and Calamine

Sample	Electrode Potential (mV)	Amount of Zn (II) or Cu (II) by ISE (ppm)	Amount of Zn (II) or Cu (II) by AAS (ppm)
Copper pyrite	195	2414	2480
Zinc blende	235	1765	1775
Calamine	234	1634	1610

6.3.2.5 Determination Of Copper And Zinc In Soils

Six Soils samples collected from different parts of India as described in chapter 2, were studied. For this 10 g of soils, S₁, S₂, S₃, S₄ S₅ or S₆ was taken in separate beakers and soil extract was prepared as the method described in chapter 2. The pH was checked for each case and it was observed that the pH was within the working range of electrode for both the metals. Then the volume was made up to 100 ml and potential were recorded (Table 6.16) using Cu(II) ISE and Zn (II) ISE and the value was converted to the concentration Cu(II) and Zn(II) of metal ions. The amount of copper content and zinc content was calculated from the calibration curve (Fig. 6.12 and 6.20) for each soil sample.

FIG. 6.19 : Determination of Zn(II) Ion in Zinc Blende and Calamine

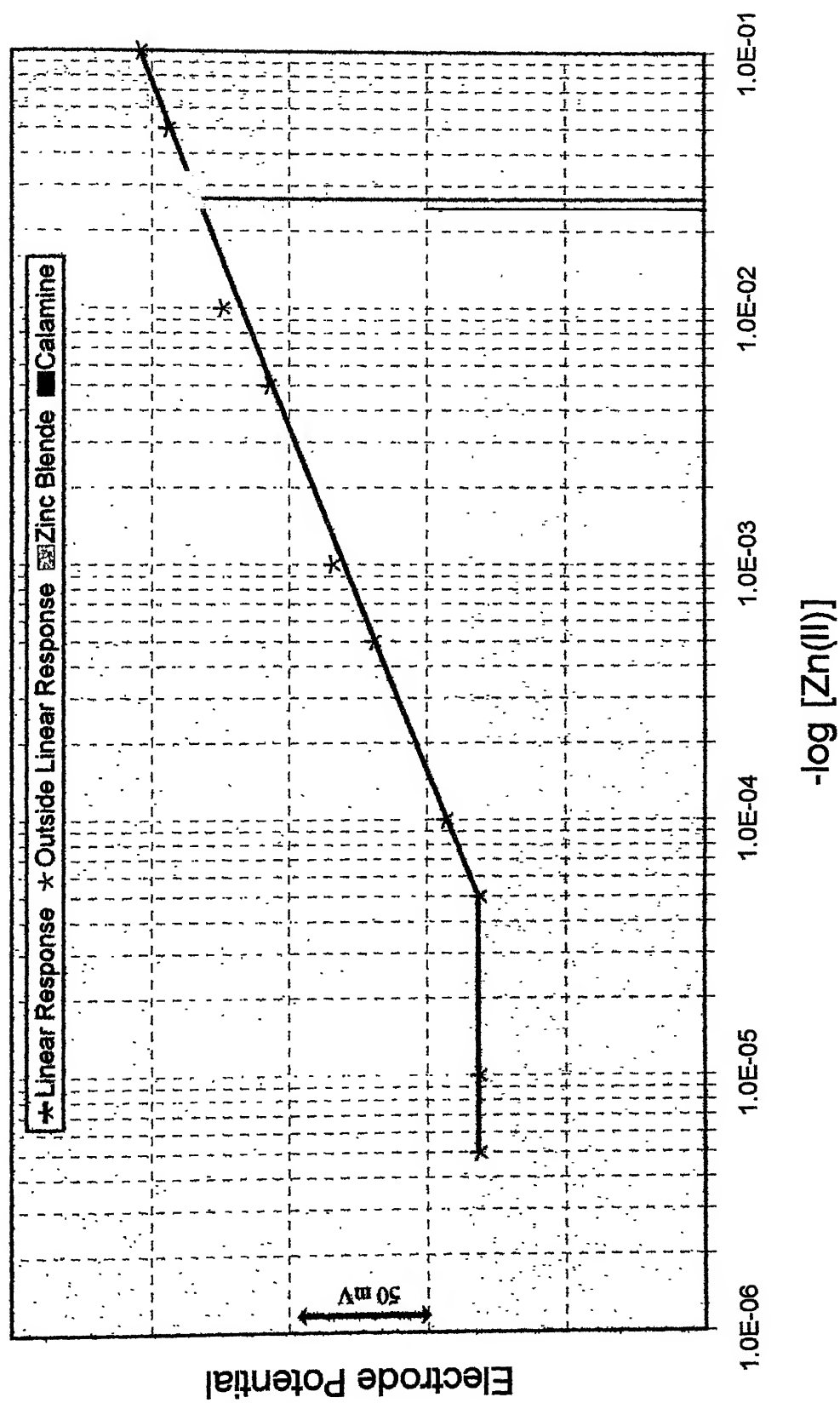
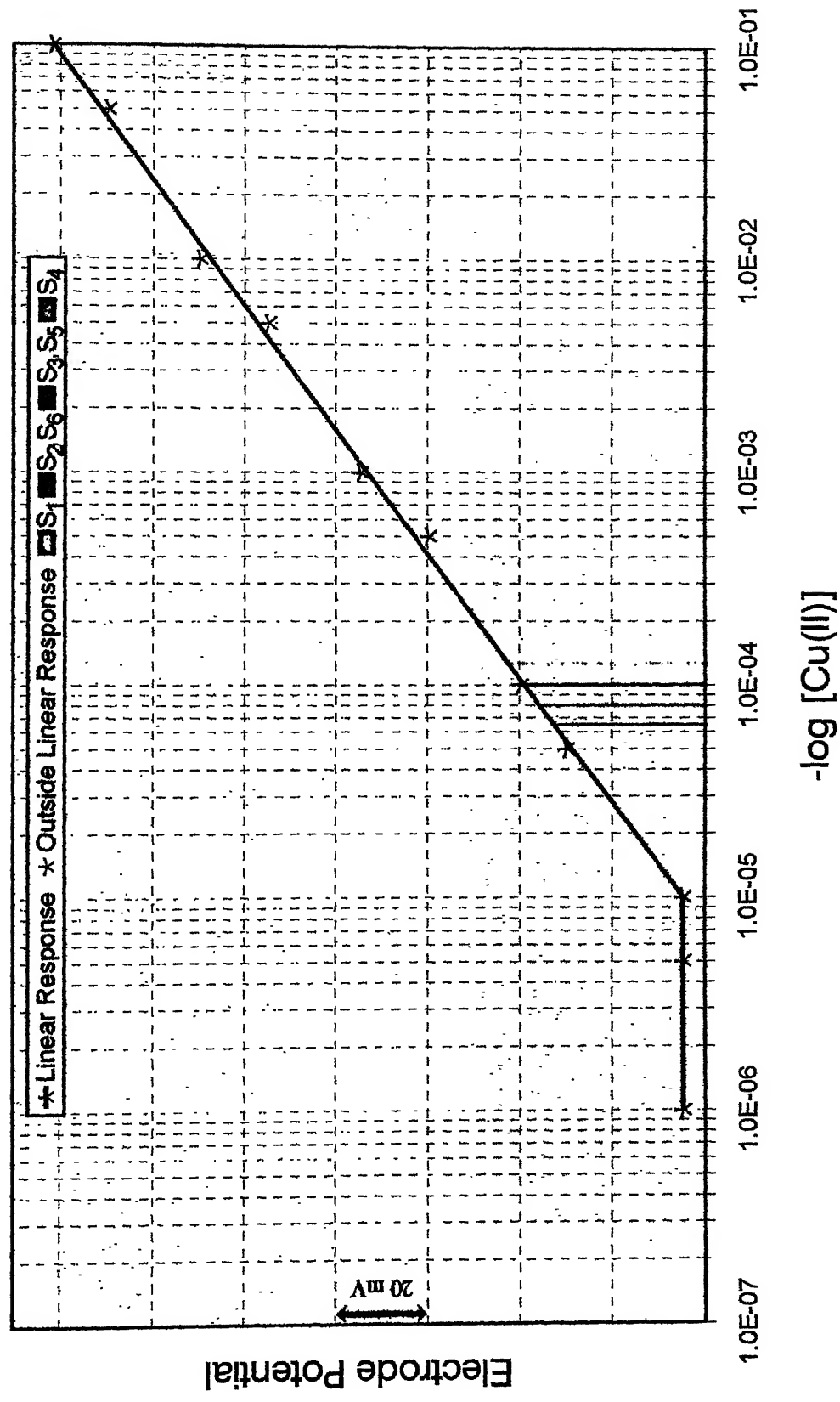


FIG. 6.20 : Determination of Cu(II) Ion in Soils



The AAS technique was also used for determination of copper and zinc content in soils at the Research and Development Laboratory, IFFCO, Phulpur. The instrument was set as:

Metal	Wavelength (λ_{max}) (NM)	Slit (nm)	Flame
Cu	324.8	0.7	Air- acetylene
Zn	213.9	0.7	Air- acetylene

The values were then recorded (Table 6.16) and it was observed that there is good agreement between the values obtained by both the techniques used.

Table: 6.16
Analysis of Soils

Soil Samples	Electrode Potential (mV)	Amount of Cu (II) by ISE (ppm)	Amount of Cu (II) by AAS (ppm)	Electrode Potential (mV)	Amount of Zn (II) by ISE (ppm)	Amount of Zn (II) by AAS (ppm)
S ₁	143	0.8	0.8	184	1.00	1.0
S ₂	140	0.6	0.6	180	0.78	0.8
S ₃	133	0.4	0.4	185	1.10	1.1
S ₄	131	0.5	0.5	183	0.91	0.9
S ₅	133	0.4	0.4	186	1.20	1.1
S ₆	140	0.6	0.6	185	1.10	1.1

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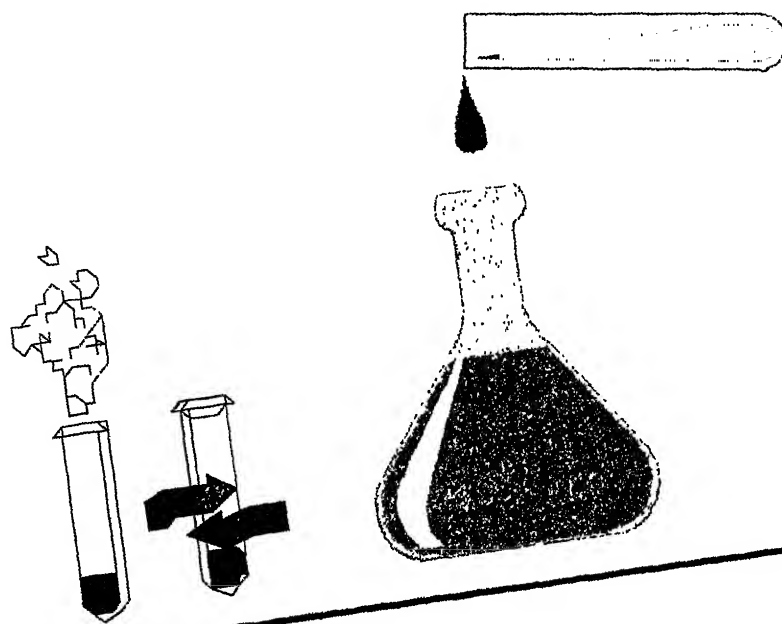
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CHAPTER 7

Summary and Conclusion



SUMMARY AND CONCLUSION

The present work deals with exploration of the analytical tool ISEs for determination of ions present in naturally occurring minerals, soil samples and synthetic materials.

The thesis has been divided into seven chapters. Chapter 1 presents an introduction to the work, and very briefly gives an account of the development of analytical chemistry and ISE technique.

The material, method and techniques adopted in the present work have been discussed in chapter 2.

The synthesis and experimental details of zeolite, potassium calcium aluminium hydrate zeolite, i.e. *willhendersonite*, $\text{KCaAl}_3\text{SiO}_2$ and synthesis of various electroactive materials used for the fabrication of ISEs have been described in chapter 3. The precipitate based electroactive materials, which were prepared, for different cations are summarized in Table 7.1.

Using these electroactive materials barrel shaped membrane based ISEs were fabricated and their characteristics in terms of linear response, response time, effect of pH, selectivity coefficient and lifetime were studied. Characteristics of all the ISEs were prepared are given in chapters 4, 5 and 6 and are summarized in Table 7.2.

Using these ISEs the metal ion contents of the following naturally occurring minerals *magnesite, dolomite, limestone, calcite, chalk, bauxite, laterite, marl, clay, basalt, galena, red lead, alum, manganite, copper pyrite, zinc blende, calamine, haematite* and *clay iron stone* were determined.

Table : 7.1
Precipitate based Electroactive Materials
for some Metal Ions

Ion	Precipitating reagent	Electroactive Material
K (I)	Sodium tetraphenyl boron	Potassium tetraphenyl boron
Ca (II)	Succinic acid	Calcium succinate
Ca (II)	Citric acid	Calcium citrate
Mg (II)	Methye orange (sodium p-dimethylamino-azo benzene sulphonate)	Magnesium p-dimethylamino-azobenzene sulphonate
Al (III)	Benzoic acid	Aluminium benzoate
Al (III)	Diphenylamine	Aluminium diphenylamine
Al (III)	Alizarin sulphonic acid	Aluminium alizarine-3-sulphonate
Pb (II)	Ammonium molybdate	Lead molybdate
Pb (II)	sodium diethyldithiocarbamate	Lead diethyldithiocarbamate
Mn (II)	Sodium diethyldithiocarbamate	Manganese diethyldithiocarbamate
Fe (II)	Quinol	Iron quinol complex
Cu (II)	Rubeanic acid	Copper rubeanate
Cu (II)	Sodium diethyldithiocarbamate	Copper diethyldithiocarbamate
Zn (II)	Uric acid	Zinc urate
Zn (II)	Sodium diethyldithiocarbamate	Zinc diethyldithiocarbamate

The metal ion contents of these minerals were also determined by either atomic absorption spectroscopy or by X-ray fluorescence. The values obtained by ISEs method are compared with the values obtained by other methods. The comparative values are given in Table 7.3, 7.4 and 7.5.

Table: 7.2
Characteristics of Metal Ion Selective Membrane Electrodes

ISE	Electroactive Material	Linear Response (mol dm ⁻³)	Slope (mV/decade) in metal ion Concentration	Response Time(Sec)	Effect of pH	Life Time (months)	Selective in presence of Ions.
K(I)	Potassium tetraphenyl boron	1 x 10 ⁻⁴	30	20	3-10	5	Na(I), Ca(II), Mg(II), Ba(II), Pb(II), Zn(II), Cu(II), Al(III)
Mg(II)	Magnesium p-dimethylamino-azobenzene sulphonate	5 x 10 ⁻⁵	33	20	2-9	4	Cu(II), Zn(II), Ni(II), Ca(II), Ba(II), Pb(II), Al(III), Fe(III).
Ca(II) Electrode I	Calcium succinate	1 x 10 ⁻⁴	44	25	1-12	5	Ba(II) Mg(II), Pb(II), Ni(II), Cu(II), Mn(II), Al(III).
Ca(II) Electrode II	Calcium citrate	5 x 10 ⁻⁵	35	20	1-12	5	
Al(III) Electrode I	Aluminium diphenylamine	1 x 10 ⁻⁴	30	15	4-11	6	Ba (II),Ca (II), Pb (II), Zn (II), Cu (II), Fe (III), Sb (II), Bi(III), Zr(IV), Th(IV)
Al(III) Electrode II	Aluminium benzoate	5 x 10 ⁻⁵	35	20	2-9	6	
Al(III) Electrode III	Aluminium alizarine-3-sulphonate	1 x 10 ⁻⁵	30	25	3-9	6	
Pb(II) Electrode I	Lead molybdate	5 x 10 ⁻⁵	35	30	2-6	6	Cu (II), Cd (II), Mn (II), Zn (II), Ca (II), Zn (II), Ca (II), Ni (II), and Al (III).
Pb(II) Electrode II	Lead diethyldithiocarbamate	1 x 10 ⁻⁵	28	30	2-6	6	
Mn(II)	Manganese diethyldithiocarbamate	5 x 10 ⁻⁵	38	30	2-7	6	Ni(II), Co(II), Cu(II), Pb(II), Fe(III), Fe(II), Al(III), Ca(II), Mg(II)
Fe(III)	Iron quinol	1 x 10 ⁻⁴	35	25	1-3	5	Pb(II), Cu(II), NaOH, K(I), Al(III), Ca(II), Mg(II)
Cu(II) Electrode I	Copper rubeanate	1 x 10 ⁻⁵	33	25	2-8	8	Ba(II), Mg(II), Ca(II), Pb(II), Mn(II), Zn(II), Co(II), Al(III), Fe(III)
Cu(II) Electrode II	Copper diethyldithiocarbamate	5 x 10 ⁻⁵	37	25	2-8	8	
Zn(II) Electrode I	Zinc urate	5 x 10 ⁻⁵	34	20	1-7	8	Cu(II), Ba(II), Mg(II), Ca(II), Pb(II), Mn(II), Co(II), Al(III), Fe(II).
Zn(II) Electrode II	Zinc diethyldithiocarbamate	1 x 10 ⁻⁵	32	30	2-7	8	

Table : 7.3
Analysis of Some Naturally Occurring Minerals

Sample	Weighed Amount of Sample(g)	Electrode Used	Metal which is Determined	Amount Determined by ISE(g)	Amount Determined by XRF(g)
Dolomite A	0.5	Mg(II)	Mg(II)	0.0608	0.0612
	0.1	Mg(II)	Mg(II)	0.1216	0.1224
Dolomite B	0.5	Mg(II)	Mg(II)	0.0729	0.0759
	0.1	Mg(II)	Mg(II)	0.1459	0.1518
Dolomite C	0.5	Mg(II)	Mg(II)	0.078	0.078
	0.1	Mg(II)	Mg(II)	0.158	0.156
Limestone	0.2	Ca(II) <i>Electrode II</i>	Ca(II)	0.0720	0.0749
	0.5	Ca(II) <i>Electrode II</i>	Ca(II)	0.1800	0.1874
Magnesite	0.5	Mg(II)	Mg(II)	21.88	21.600
Calcite	0.5	Ca(II)	Ca(II)	520	500
Chalk	0.2	Ca(II)	Ca(II)	200	200
Bauxite A	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.0540	0.0575
	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.1350	0.1437
Bauxite B	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.6480	0.0620
	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.1485	0.1549
Bauxite C	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.0702	0.0647
	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.1620	0.1685
Laterite	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.0068	0.0077
	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.0162	0.0192
	1.0	Al (III) <i>Electrode I</i>	Al (III)	0.0336	0.0384
Clay	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.0338	0.0315
	1.0	Al (III) <i>Electrode I</i>	Al (III)	0.0675	0.0630
Basalt	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.0054	0.0060
	0.5	Al (III) <i>Electrode I</i>	Al (III)	0.0149	0.0150
	1.0	Al (III) <i>Electrode I</i>	Al (III)	0.0297	0.0300
Marl	2.0	Al (III) <i>Electrode I</i>	Al (III)	0.0540	0.0578
	3.0	Al (III) <i>Electrode I</i>	Al (III)	0.0810	0.0867

Table : 7.4
Analysis of Red Lead and Alum

Sample	Weighed Amount of Sample (g)	Electrode Used	Metal which is Determined	Amount Determined by ISE (g)	Actual Value (g)
Alum	0.2	Al (III) <i>Electrode I</i>	Al (III)	0.0105	0.0113
Red Lead	0.1	Pb (II) <i>Electrode II</i>	Pb (II)	0.0932	0.0906
	0.2	Pb (II) <i>Electrode II</i>	Pb (II)	0.1864	0.1813
	0.5	Pb (II) <i>Electrode II</i>	Pb (II)	0.4144	0.4532

Table : 7.5
Analysis of Some Naturally Occurring Minerals

Sample	Weighed Amount of Sample (g)	Electrode Used	Metal which is Determined	Amount Determined by ISE (ppm)	Amount Determined by AAS (ppm)
Manganite	1.0	Mn (II)	Mn (II)	142	140
Haematite	0.2	Fe (III)	Fe (III)	1256	1248
Clay Iron Stone	1.0	Fe (III)	Fe (III)	1452	1440
Copper Pyrite	1.0	Cu (II) <i>Electrode II</i>	Cu (II)	2414	2480
Zinc Blende	1.0	Zn (II) <i>Electrode I</i>	Zn (II)	1765	1775
Calamine	1.0	Zn (II) <i>Electrode I</i>	Zn (II)	1634	1610
Galena	0.1	Pb (II) <i>Electrode II</i>	Pb (II)	0.0746	0.0782
	0.2	Pb (II) <i>Electrode II</i>	Pb (II)	0.1450	0.1564
	0.5	Pb (II) <i>Electrode II</i>	Pb (II)	0.4144	0.3910

A number of soil samples were collected from the various parts in India are also studied. The collection sites are:

S_1 (Allahabad), S_2 (Agra), S_3 (Allahabad), S_4 (Sonbhadra), S_5 (Panchgani) and S_6 (Panchmarhi).

ISEs developed in the present work determined the metal ion contents in these soil samples and values thus obtained are compared with the values obtained by AAS.

For comparison of metal ion content in these soil samples a bar diagram was drawn (Table 7.6, 7.7 and Fig. 7.1).

It is concluded that all the six soil samples contain very high amount of iron content in comparison to other metal ions while the lead content is present in very small quantity. The lead contents in soil S₁ and S₆ are absent. The calcium and copper contents are also very low in all the soil samples. The amount of zinc and manganese content is almost equal. Potassium and magnesium are present almost equal quantity in all the soil samples. But soil S₅ and S₆ contain very low potassium content in comparison to other soils, which are studied. Both the methods, which are applied throughout the course of study show there is good agreement between the values.

Table : 7.6
Analysis of Soil Samples by ISE Method

Soil Samples	Amount of K(I) (ppm)	Amount of Mg (II) (ppm)	Amount of Ca (II) (ppm)	Amount of Pb (II) (ppm)	Amount of Mn (II) (ppm)	Amount of Fe (III) (ppm)	Amount of Cu (II) (ppm)	Amount of Zn (II) (ppm)
S ₁	10.92	15.80	4.8	0.000	3.2	42.0	0.8	1.00
S ₂	10.14	15.59	—	—	4.3	44.6	0.6	0.78
S ₃	19.50	17.00	5.6	—	4.1	72.0	0.4	1.10
S ₄	7.800	12.16	—	0.312	2.7	52.0	0.5	0.91
S ₅	—	13.37	—	0.589	6.5	92.0	0.4	1.20
S ₆	—	14.01	—	0.000	5.4	84.0	0.6	1.10

FIG. 7.1 : Metal Analysis of Various Soils

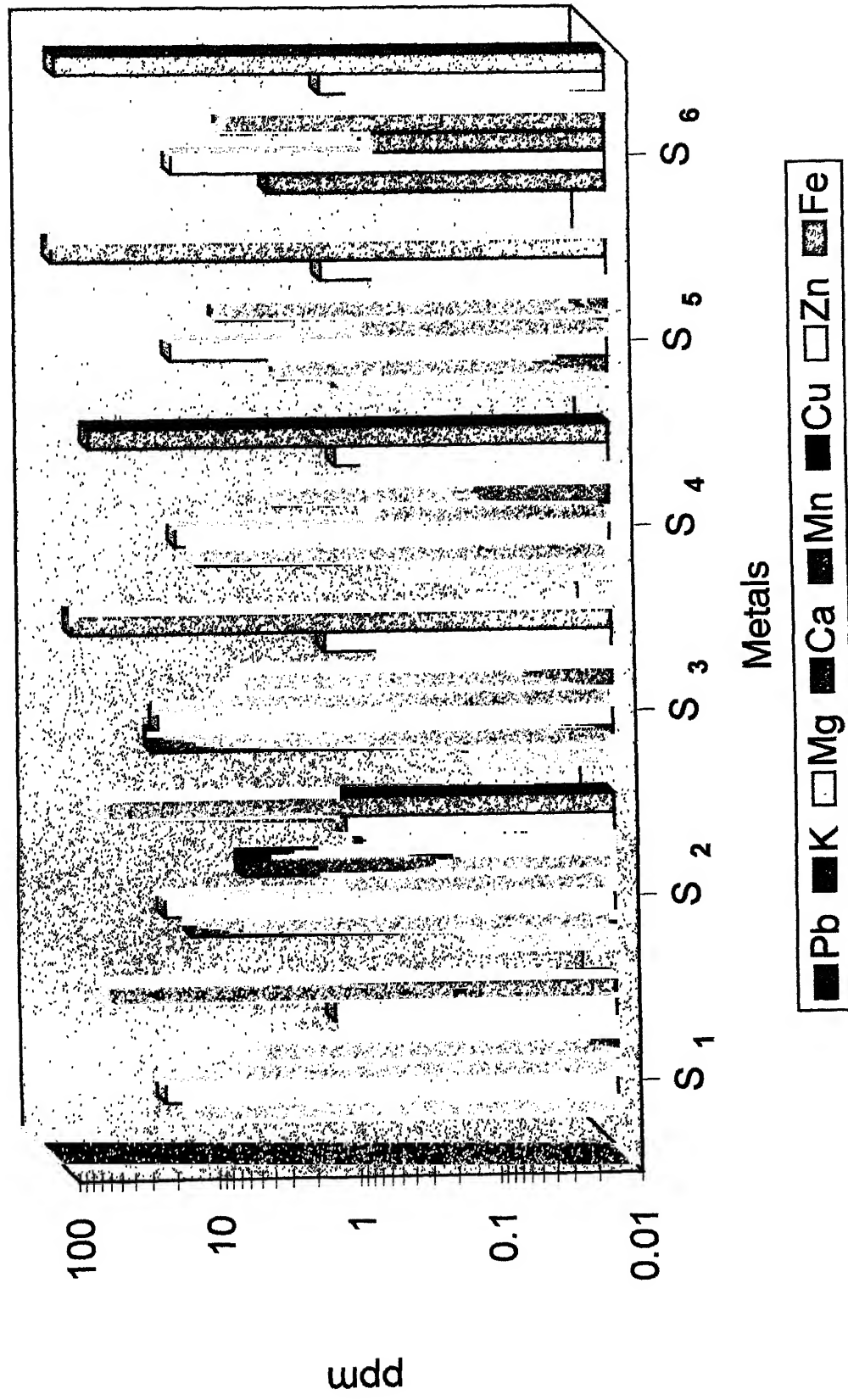


Table : 7.7
Analysis of Soil Samples by AAS Method

Soil Samples	Amount of K(I) (ppm)	Amount of Mg (II) (ppm)	Amount of Ca (II) (ppm)	Amount of Pb (II) (ppm)	Amount of Mn (II) (ppm)	Amount of Fe (III) (ppm)	Amount of Cu (II) (ppm)	Amount of Zn (II) (ppm)
S ₁	10.60	16.30	4.6	0.0	3.4	42.0	0.8	1.0
S ₂	10.20	15.80	0.9	0.1	4.3	44.6	0.6	0.8
S ₃	19.00	17.40	5.3	0.1	4.2	72.0	0.4	1.1
S ₄	08.80	12.60	0.5	0.3	2.6	52.0	0.5	0.9
S ₅	02.20	13.30	0.8	0.8	6.1	92.0	0.4	1.1
S ₆	02.60	13.80	0.5	0.0	5.5	84.0	0.6	1.1

The application of seven ISEs namely K(I), Mg(II), Ca(II), Pb(II), Mn(II), Cu(II) and Zn(II), were also explored as an indicator electrode in the precipitation titration. The titration performed with these ISEs are summarized in Table 7.8.

Table : 7.8
Potentiometric Precipitation Titration.

Ion for which Electrode is Selective	Titration
K (I)	Titration of potassium nitrate against sodium tetra phenyl borate
Mg (II)	Titration of magnesium chloride against disodium hydrogen phosphate.
Ca (II)	Titration of calcium choride against sodium palmitate.
Pb (II)	Titration of lead nitrate against potassium chromate.
Mn (II)	Titration of manganese chloride against diammonium hydrogen phosphate.
Cu (II)	Titration of copper sulphate against EDTA.
Zn (II)	Titration of zinc chloride against potassium ferrocyanide.

During the course of entire work fifteen ISEs for nine cations were prepared and it was found that the results obtained are very satisfactory and it can be concluded that these electrodes are stable, as fairly good lifetime and are selective for respective metal ions.

These ISEs could be used both as an indicator electrode in the precipitation titration as well as in the direct determination of respective ions in naturally occurring mineral solutions.

